Polychromy on wooden lacunar ceiling: the case study of Bagatti Valsecchi Palace (Milan, Italy)

A. Sansonetti[1], S. Della Torre[2] and L. Rampazzi[3]

[1] C.N.R. – ICVBC – Sezione 'Gino Bozza', Milan, Italy
[2] Department BEST, Politecnico of Milan, Milan, Italy
[3] Department of Chemical and Environmental Sciences, University of Insubria, Como, Italy

Key words: polychromy, wood, ceilings, monitoring

Introduction and content

Bagatti Valsecchi Palace in Milan is a house-museum built in 19th century, which resembles architectural elements of 16th Century dwelling-places of the Lombard aristocracy. The important collection of Renaissance art and antiquities, in particular paintings and furniture, is placed in rooms decorated by polychrome wooden ceiling panels; geometrical and floral subjects constitute the decorating pattern.

The palace has recently undergone a diagnostic campaign, focused on the definition of building techniques and degradation phenomena of the architectural elements; the wooden lacunar ceiling has been deeply surveyed. Its good state of conservation was an unique opportunity to investigate its features, seldom described in scientific literature. Aim of this work has been the identification of the painting materials, i.e. pigments and binding media, and of the decay products, and to correlate data contained in "Art and Crafts" handbooks published in the beginning of the XX century [1-6] with analytical findings.

Various analytical approaches have been undertaken, such as chromatography, microscopical and spectroscopic investigations. The knowledge about the painting techniques, linked to the state of conservation detected, has been used to plan conservation strategies; a correct suggestion indicates monitoring as the most useful method to grant the best equilibrium between conservation and use, according to the museum designation of the building.

Table 1: Description of the samples coming from the lacunar ceiling (on the right)

Sample	*Description*
1	Efflorescence
2	Polychrome layer
3	Polychrome layer
4	Polychrome layer
5	Polychrome layer
6	Polychrome layer
7	Polychrome layer
8	Polychrome layer
9	Surface deposit

Analytical results

Fragments of polychrome wooden ceiling panels were sampled by means of a lancet, according to the indication of the UNI- Normal protocols (Table 1).

After the preliminary observations at a Leitz stereomicroscope, samples polished cross sections were investigated by Optical Microscopy and by Scanning Electronic Microscopy equipped with X-ray spectrometer (SEM -EDX, JEOL 5910 LW).

The finishing layers were carefully sampled under a stereomicroscope by means of a needle-sampler and analysed in a diamond cell by Fourier Transformation Infrared Spectroscopy (FTIR, Nicolet, transmission mode, 400-4000 cm^{-1}, 4 cm^{-1} resolution).

The samples were also ground in an agate mortar as to obtain homogeneous powders for the different analyses by means of Powder X-Ray Diffraction (XRD, diffractometer Philips, diffraction files range 3°-65° (1°/min), CuKα radiation) and Ionic Chromatography (Dionex, anion analysis by PacAS4A column, after extraction in ultra-pure water).

The optical observations allowed to describe polychrome layers and to plan the following analytical investigations. XRD and FTIR spectra were able to clarify the nature of the compounds, both inorganic and organic, while SEM-EDS analyses were useful in studying the morphology and the element composition of the samples, decisive in some cases for the determination of the pigments present in a specific layer.

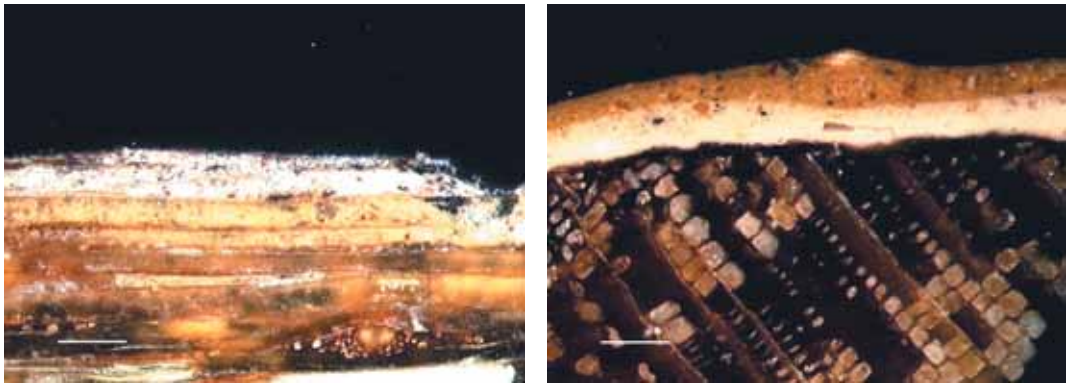

Figure 1: Stratigraphies of a complex sequence of layers (left) and a simple one (right)

In case of samples 3, 5 and 6, the wooden substrate is simply covered by an unique finishing layer (Figure 1, right): in sample 3 and 6 gypsum, calcite, calcium oxalate and organic compounds – probably proteinaceous substances used as binders – were detected. The brownish colour is due to the presence, respectively, of ochre and of a mixture of zinc white, barite and ochre. Sample 5 was composed by clays, lead white and organic compounds, whose reliable determination was not possible. In other cases a more complicated stratigraphy was observed and carefully analysed (Figure 1, left). The internal layer, generally white or ochre, was composed by gypsum, sometimes added with lead white (sample 7) or with a mixture of calcite, zinc white and ochre (sample 2). In the external layer, i.e. the finishing brownish one, gypsum, calcite and organic compounds were found. In case of sample 7 the brownish colour was due to the presence of yellow ochre, lead white and titanium white. The intermediate layer observed in sample 2 contains gypsum. As an example, Figure 2 shows the FTIR spectrum of the external layer of sample 7, presenting the peculiar peaks of gypsum, calcite, organic compounds and yellow ochre. EDX spectrum confirmed the results, with the characteristic signals of aluminium, silicon, calcium; lead and titanium suggested the presence of lead white and titanium white (Figure 3).

The stratigraphy of sample 4 revealed four layers. Analysing the sequence from the wood substrate to the finishing, the first two layers, respectively greyish and whitish, showed the

presence of gypsum and organic compounds, while the third presented a red coloration obtained by a mixture of gypsum, calcite, lead white, ochre and an organic binder. The finishing, once again brownish, presented lead white, calcite and titanium white.

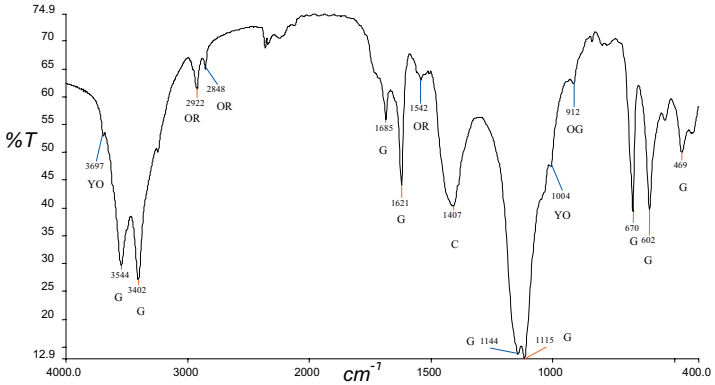

Figure 2: FTIR transmission spectrum of sample 7 /intermediate layer showing the absorbance peaks of gypsum (G), calcite (C), yellow ochre (YO), organic compounds (OR)

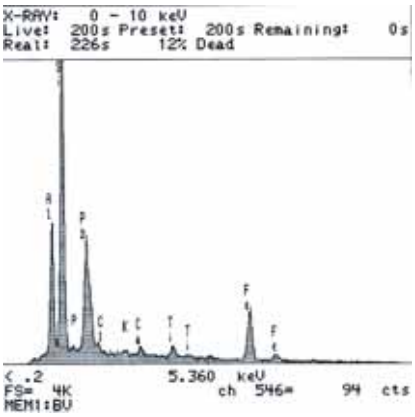

Figure 3: EDX spectrum of sample 7 /intermediate layer showing the peaks of aluminium, silicon, calcium, lea, iron and titanium

As far as the degradation products are concerned, XRD analysis of sample 1 (efflorescence) indicated the presence of thenardite (sodium sulphate), calcite (calcium carbonate) and silicates. High amounts of sulphates and nitrates were determined by IC analyses. Deposit (sample 9) was composed by barium sulphate, nitrates and traces of organic compounds, as shown by FTIR spectra.

Conclusions

Eclectic architecture has not yet deeply investigated for what regards material used in finishing especially if a wooden substrate is concerned. This represents a problem to plan a correct conservation work. Renewed care and attention to these kind of architectural heritage ask for the acquisition of compositional data, linked to a complete investigation of the vast collection of handbooks which in those years have been published in the flourishing of Industrial Art.

The examined finishing on the wooden ceiling does not show a homogeneous composition, even if in the most of the cases a mixture of lime and gypsum has been revealed; barite, lead white, titanium white and zinc white have been as well individuated. These kinds of mixtures are to be linked to early industrial production. A survey carried out on handbooks of the period informed that lime and gypsum have been used as the main components with the role of thickening; on the contrary other white pigments have been used to increase hiding power (titanium oxide or lead white), or to enhance transparency (barite). At the period a medium prepared with egg yolk was still used, witnessing the conservation of traditional painting techniques with more innovative materials such as titanium white.

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THE PROBLEM OF THE ORGANIC MATERIALS IDENTIFICATION IN WALL PAINTINGS: TESTING PROCEDURES

Elisa Campani, Antonella Casoli
Dipartimento di Chimica Generale e Inorganica, Chimica Analitica, Chimica Fisica,
Università di Parma, V.le G. P. Usberti 17/a, 43100 Parma (Italy)

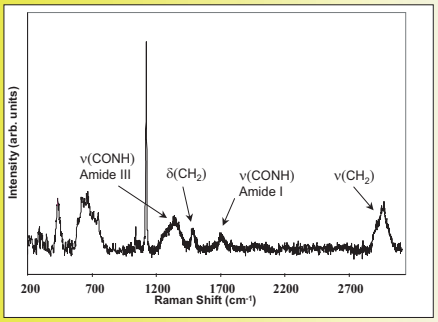
The knowledge of the different types of organic materials in wall paintings and their behavior is fundamental for the development of suitable conservation and maintenance procedures.
This research is part of an international project, coordinated by Getty Conservation Institute of Los Angeles, that aims to develop a protocol for the identification of organic materials in wall paintings, using not-invasive, not-destructive and destructive techniques.
The techniques were tested on some known composition replicas coming from Laboratorio per l'Affresco di Vainella (Centro Tintori – Prato, Italy) and each analytical technique will be evaluated in its potential and limits for identification of organic materials in wall paintings.

Z8 and Z9 tiles constituted of yellow ochre mixed respectively with egg and milk in different amount

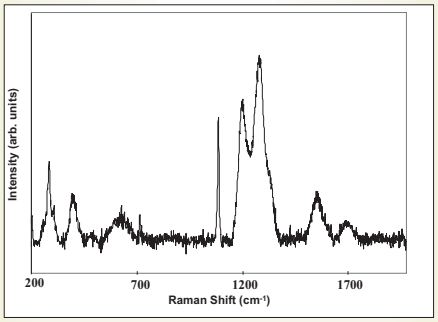
About our research we had the availability of forty-three samples made using phases of application historically used (*a fresco* over fresh plaster, *su intonaco stanco* over semi-dried plaster, and *a secco* over dry plaster), different pigment (mineral, natural, artificial) and binding media (linseed and walnut oil, egg, animal glue, milk and arabic gum) combinations.

OL17bis and OL18bis tiles constituted of linseed oil mixed respectively with egg and rabbit skin glue and a different pigments incompatible with fresh plaster

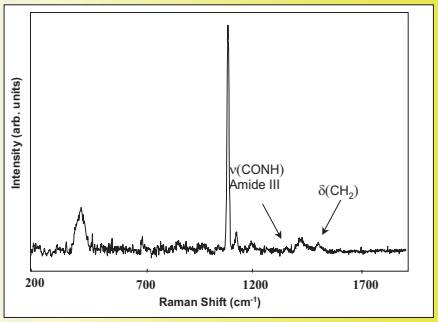
Our project part provided the use of Raman micro-spectroscopy, testing two different laser source, and gas chromatography/mass spectrometry through use of methodologies for proteinaceous[1], lipidic[2] and polysaccharides[3] materials identification.
Raman micro-spectroscopy is a not-destructive technique that allowed to detect organic material presence on some studied samples, but it does not distinguish the typology of binder employed.



Sample Z8A1 Raman spectrum obtained using 632.8 nm laser source; attributions of major bands of organic material present in the sample (egg) are high-lighted

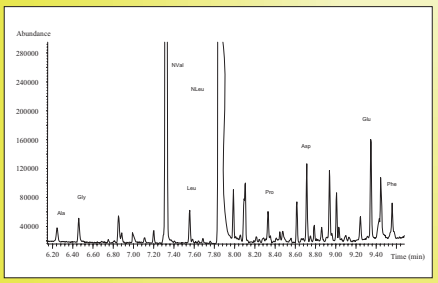


Sample Z9A1 Raman spectrum obtained using 784.8 nm laser source; it shows presence of high intensity band probably due to fluorescence phenomena

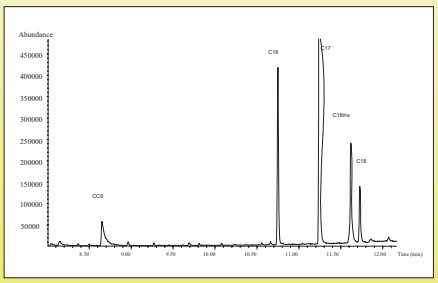


Sample OL17A1 Raman spectrum obtained using 784.8 nm source; attributions of major bands of organic material used as binding media (mix of egg and linseed oil) are high-lighted

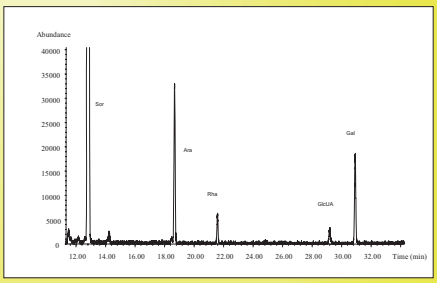
To classify the organic binding media was used gas chromatography/mass spectrometry that allowed to confirm a lot of expected results. For example chromatograms of some analysed samples are showed: Z8A1 containing egg, OL17A1 containing linseed oil mixed with egg and AZ1D1 containing arabic gum, walnut oil and animal glue.



Chromatogram of sample Z8A1 proteinaceous fraction: Ala = alanine, Gly = glycine, Nval = norvaline (i.s.), Leu = leucine, Nleu = norleucine (i.s.), Pro = proline, Asp = aspartic acid, Glu = glutamic acid, Phe = phenilalanine



Chromatogram of sample OL17A1 lipidic fraction: CC9 = azelaic acid, C16 = palmitic acid, C17 = eptadecenoic acid (i.s.), C18ins = oleic and linoleic acid, C18 = stearic acid



Chromatogram of sample AZ1D1 polysaccharidic fraction: Sor = sorbitole (i.s.), Ara = arabinose, Rha = rhamnose, GlcUA = glucuronic acid, Gal = galattose

Casoli, A.; Musini, P.C; Palla, G. *A gas chromatographic-mass spectrometric approach to the problem of characterizing binding media in paintings.* J. Chromat. A, *731*, **1996**, *19*, 273-246.
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Casoli, A.; Cremonesi, P.; Palla, G.; Vizzarri, M. *Application of Gas Chromatographic-Mass Spectrometry analysis to the study of works of art: paint media identification in polychrome multi-material sculptures*; Annali di Chimica, *91*, **2001**, 727-739.

The problem of organic materials identification in wall paintings: testing procedures

Elisa Campani and Antonella Casoli

Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica e Chimica Fisica, Università di Parma, Viale G. P. Usberti 17/A, Parma (Italy)

Key words: wall paintings, binding media, micro-Raman spectroscopy, gas chromatography / mass spectrometry

Introduction and content

The knowledge of the different types of organic materials in wall paintings and their behaviour is fundamental for the development of suitable conservation and maintenance procedures.

This research is part of an international project *Organic Materials in Wall Paintings* (OMWP) coordinated by the Getty Conservation Institute of Los Angeles, that aims to develop a protocol for the identification of organic materials in wall paintings, starting from non-invasive e non-disruptive investigation to disruptive sampling and testing procedures. The techniques were tested on some known composition replicas coming from Laboratorio per l'Affresco di Vainella (Centro Tintori – Prato, Italy) (LAV replicas) and each analytical technique will be evaluated in its potential and limits for identification of organic materials in wall paintings.

The main objective of this work is to develop a methodology for the identification of the organic materials in wall paintings starting from Micro-Raman spectroscopy and gas chromatography / mass spectrometry. LAV replicas were to be used as samples of known composition for the investigation set up and for testing of the methodology in its various components.

About our research we had the availability of forty-three samples made using phases of application historically used (*a fresco* over fresh plaster, *su intonaco stanco* over semi-dried plaster, and *a secco* over dry plaster), different pigment (mineral, natural, artificial) and binding media (linseed oil, walnut oil, egg, animal glue, milk and arabic gum) combinations.

Our project part provided the use of Raman micro-spectroscopy, testing two different laser source [1], and gas chromatography / mass spectrometry through use of methodologies for proteinaceous [2], lipidic [3] and polysaccharides [4] materials identification.

Raman micro-spectroscopy is a not-destructive technique that allowed to detect organic material presence on some studied samples, but it does not distinguish the typology of binder employed. For example Raman spectrum of a sample containing only egg, obtained by use of red laser line at 632.8 nm (He-Ne laser-max power 20 mW) is presented in figure 1. Whole egg protein shows amide I (~1657 cm^{-1}), CH_2 scissoring (~1440 cm^{-1}) and amide III (~1290 cm^{-1}) bands. The same sample was studied by a near-infrared laser at 784.8 nm (laser diode-max power 30 mW) to minimise the interferences caused by the fluorescence background. In this case the spectrum shows some high intensity bands probably because of binding medium chromophor groups.

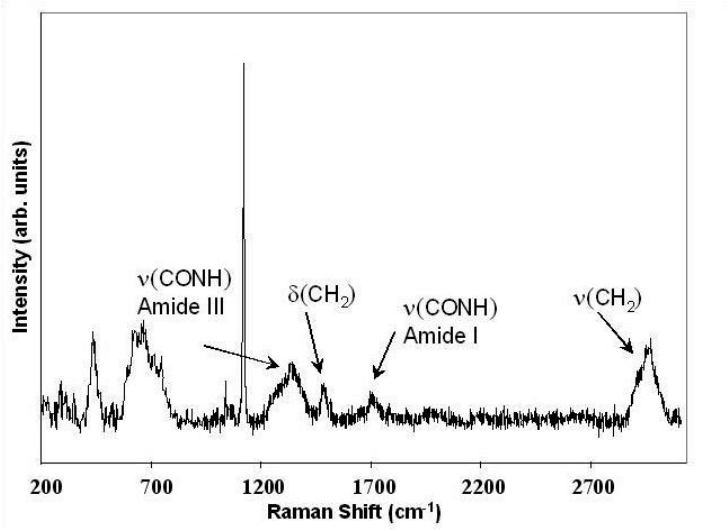
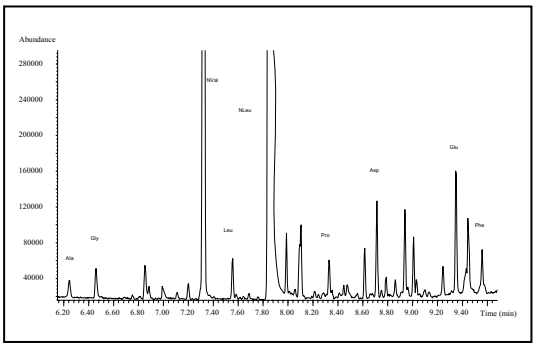
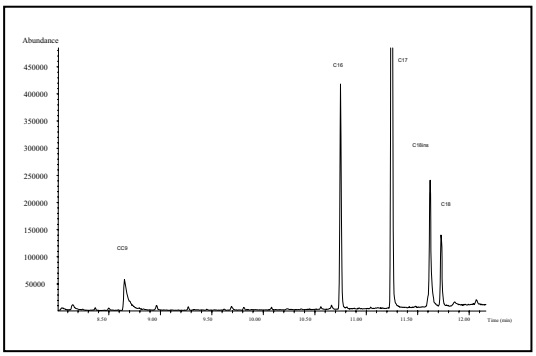


Figure 1: Sample Z8A1 Raman spectrum obtained using 632.8 nm laser source; attributions of major bands of organic material present in the sample (egg) are high-lighted

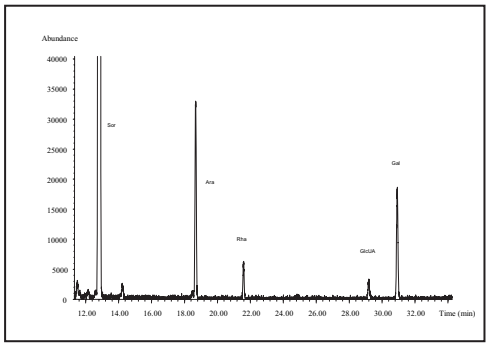
To classify the organic binding media gas chromatography / mass spectrometry was used. This technique allowed to know the composition of the LAV replicas, confirming the expected results. For example, chromatograms of some analyzed samples are showed: Z8A1 containing egg, OL17A1 containing linseed oil mixed with egg and AZ1D1 containing arabic gum, walnut oil and animal glue.



Chromatogram of sample Z8A1 proteinaceous fraction: Ala = alanine, Gly = glycine, Nval = norvaline (i.s.), Leu = Leucine, Nleu = norleucine (i.s.), Pro = proline, Asp = aspartic acid, Glu = glutamic acid, Phe = phenilalanine



Chromatogram of sample OL17A1 lipidic fraction: CC9 = azelaic acid, C16 = palmitic acid, C17 = eptadecenoic acid (i.s.), C18ins = oleic and linoleic acid, C18 = stearic acid



Chromatogram of sample AZ1D1 polysaccharidic fraction: Sor = sorbitole (i.s.), Ara = arabinose, Rha = rhamnose, GlcUA = glucuronic acid, Gal = galattose

European dimension

The identification of organic materials in wall paintings is an important step in any conservation program. Three main reasons can be identified as follow:

Art historical: To support the study of the development of mural painting techniques and advance our understanding of artistic intent.
Diagnostic: To contribute to the knowledge required for the understanding of the processes of mural deterioration.
Treatment: To provide the basic knowledge to develop a compatible conservation intervention in term of methods and material.

Innovation and originality

The OMWP international project grows up from the need to develop an analytical protocol for the characterization of the organic material in wall painting technique. The application of the analytical methodologies to real case studies (a component of this project) will help illustrate the procedure and highlight the implication that the presence of organic materials has in wall paintings conservation. The dissemination and use of the methodology will show how wall paintings are often more complex in their execution technique than what we think.

Impacts

The developed protocol improves the study of the organic materials in wall paintings. In particular, the same paint sample can be studied, at different knowledge levels, by Micro-Raman spectroscopy and gas chromatography / mass spectrometry.

Acknowledgement

The authors thank the Getty Conservation Institute (Los Angeles) that allowed us to contribute to this interesting project.

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X-RAY FLUORESCENCE ANALYSIS AND ITS USE FOR CZECH MEDIEVAL FRESCOS

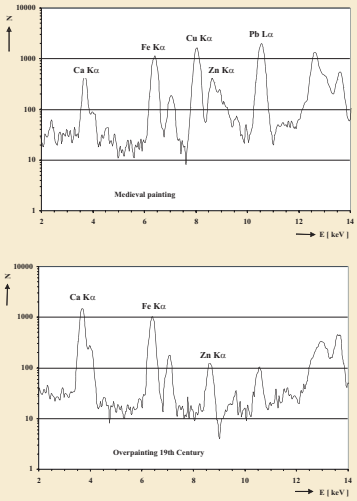
Tomáš Čechák[1], Ivana Kopecká[2], Ladislav Musílek[1], Tomáš Trojek[1]

[1] Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering, Břehová 7, 115 19 Praha 1, Czech Republic
[2] National Institute for the Care and Preservation of Historic Monuments and Sights, Valdštejnské nám. 3, 118 01 Praha 1, Czech Republic

Introduction

X-ray fluorescence analysis (XRFA) of frescos in Czech castles and churches has been carried out for the purposes of art history and monument care and restoration. Monuments from the Czech cultural heritage that have been investigated include: the Late Gothic frescos in the palace and chapel of Žirovnice Castle (13th century Gothic castle in S.E. Bohemia, rebuilt in the 2nd half of the 15th century, again rebuilt and newly fortified in the 16th century), frescos in the Chapel of Our Lady and on the staircase to the Holy Cross Chapel at Karlštejn Castle (14th century Gothic Castle built by Emperor Charles IV, about 15 miles S.W. of Prague, substantially restored in the 19th century), frescos in the Church of Our Lady before Týn (Gothic church in the Old Town of Prague from the 2nd half of the 14th century, with many Baroque supplements). The results not only differentiate between the old parts of the frescos and the later repainting, but also provide some information about the types of pigments used by the medieval painters.

Detail of the fresco from Žirovnice castle



XRF spectrum of the black pigments on the fresco on the Karlštejn castle

Experimental techniques

The Si(Li) detector for in-situ measurements and the radioisotope sources ^{55}Fe, ^{238}Pu, and ^{241}Am are used. ^{55}Fe enables the excitation of elements with low Z up to 23, ^{238}Pu is used for excitation of elements with Z from 20 up to 39, and ^{241}Am is used for excitation of the K shell electrons of elements with higher Z up to 68. The Si(Li) detector is cooled by liquid nitrogen from the 5 l Dewar vessel. For special purposes, the 2 l Dewar vessel is available. These small Dewar vessels and the portable multichannel analyser enable in-situ measurements.

Si(Li) detection equipment during the measurement of the fresco from Karlštejn castle

At Karlštejn Castle our task was to date particular parts of the frescos restored in the 19th century, during the reconstruction of the castle. An analysis of the XRF spectra of the pigments is able to provide information about the type of pigments. The 14th century painters used different types of pigments than painters in the 19th century, and the application of XRFA enables us to differentiate the mediaeval and new parts of the fresco.

The red and black pigment was used as a marker of the mediaeval part of the fresco. The red pigment used in the 14th century was a mixture of Vermilion, Saturn Red, and Red Ochres. Red Ochres with Chinese White were used as a red pigment in the 19th century. An admixture of Mars Black with Saturn Red and Verdigris was used for tinting the black pigment in the 14th century. This pigment differs from the black pigment used in the 19th century (Mars Black with traces of Zn).

Detail of the fresco from St. Hyeronymus was discovered in the Church of Our Lady before Týn

The Late Gothic frescos in the palace and chapel of Žirovnice Castle were investigated. Local common pigments, e.g., Green Earth and Yellow Ochres, were used together with expensive imported pigments such as Vermilion, Saturn Red and Azurite and with pigments which were only rarely used in the fresco paintings, e.g., Antimonate Yellow, and Manganese Brown.

The mediaeval fresco of St. Hieronymus was discovered in the Church of Our Lady before Týn behind a Baroque side altar. This fresco was unique not only for its preserved state, but also for the techniques used: It was a classical fresco painted without organic materials. The investigation confirmed pigments commonly used in this period: Iron Oxide Reds and Red Ochres, Azurite, Malachite and Lead White.

Conclusion

Analyses of the pigments used by artists in the past can provide a great deal of new information as more investigations are made. Better knowledge of this heritage is very desirable and can also help to find mutual influences with other European regions.

X-ray fluorescence analysis and its use for Czech medieval frescos

Tomáš Čechák[1], Ivana Kopecká[2], Ladislav Musílek[1] and Tomáš Trojek[1]

[1] Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering, Břehová 7, 115 19 Praha 1, Czech Republic
[2] National Institute for the Care and Preservation of Historic Monuments and Sights, Valdštejnské nám. 3, 118 01 Praha 1, Czech Republic

Key words: X-ray fluorescence analysis, Si(Li) detectors, portable spectrometers, energy dispersive analysis, fresco paintings

Introduction and content

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European dimension

Due to the political developments in Europe after World War II, the Czech cultural heritage, though comparable in value with the heritage in the West European countries, is much less known and less has been written about it. Deep studies of artistic and cultural monuments in the Czech Republic can help them to regain their place in the European cultural heritage. In recent years, investigations of cultural monuments have been increasingly influenced by the introduction of methods based on the natural sciences into the spectrum of useable procedures. XRFA is one of the most successful methods, and has been applied to a variety of objects for qualitative and quantitative elemental analysis. Compared with other techniques, XRFA has the advantage of being non-destructive, multi-elemental, fast, and cost-effective. Portable equipment can be built and used for measurements in situ, without any sampling. For these reasons, XRFA is a very suitable method for analyses of many objects of the cultural heritage, and especially objects that cannot be moved into a laboratory, e.g. fresco paintings.

Innovation and originality

We have built an XRF analyser with changeable radionuclide sources in the measuring head and with an Si(Li) detector for in-situ measurements. The radioisotope sources ^{55}Fe, ^{238}Pu, and ^{241}Am are used. ^{55}Fe enables the excitation of elements with low Z up to 23, ^{238}Pu is used for excitation of elements with Z from 20 up to 39, and ^{241}Am is used for excitation of the K shell electrons of elements with higher Z up to 68. The Si(Li) detector is cooled by liquid nitrogen from a 5 l Dewar vessel. For special purposes, a 2 l Dewar vessel is available. These small Dewar vessels and the portable multichannel analyser enable in situ measurements. The collimator system of the exited radiation enables the irradiated area to be selected. Our

spectrometer can be used for area mapping and also for line scanning. The detector is equipped with an XYZ-stage, which enables maximum movements of up to 250 mm in the YZ direction.

Impacts

The pigment compositions in fresco paintings vary with the locality and date. White, for example, may be produced with Pb, Zn and Ti oxides, but ZnO was not produced before 1870, and Titanium White was not used before 1920 [1]. Therefore, if either Zn or Ti is found in the white areas of supposed fresco paintings from the Renaissance period, those paintings have been restored or they are forgeries. A more subtle study of several fresco paintings of a particular artist in order to determine the pigments characteristically used by him or his disciples will reveal frescos that were particularly typical of the artist and possibly, the times. Differences between countries or areas and time periods will most certainly be revealed, and differences between the works of fresco artists in the same place and in the same time period may also show up.

The overall results of XRFA on frescos are multielement spectra indicating the main elements of the pigments that are present. This step usually makes it possible to identify specific inorganic pigments. Several measurements have been carried out directly in the field in order to verify the method and to obtain information about Gothic fresco paintings. The valuable fresco paintings at Žirovnice Castle were investigated in this way. We were surprised to find that many pigments not typical for the region of Bohemia at the end of 15th century were used in these frescos. For all basic paints, a few pigments and combinations of pigments were used. Local common pigments, e.g., Green Earth and Yellow Ochres, were used together with expensive imported pigments such as Vermilion, Saturn Red and Azurite and with pigments which were only rarely used in the fresco paintings, e.g., Antimonate Yellow, and Manganese Brown. As in some other works of art, e.g. in Italy, artists took into consideration not only the colour and shade of the pigments but also the significance of the imaginary persons and their position in the church hierarchy. The most expensive pigments and gilding were used on the vestures of most important figures. Other less important persons and architecture were painted only with ochres. The fresco paintings at Žirovnice Castle have never been repainted and the first restoration dates to 1997-2000. During the restoration, an investigation of the frescos by XRFA was performed. A comparison of the X-ray spectra from the fresco paintings at Žirovnice Castle is shown in Fig. 1.

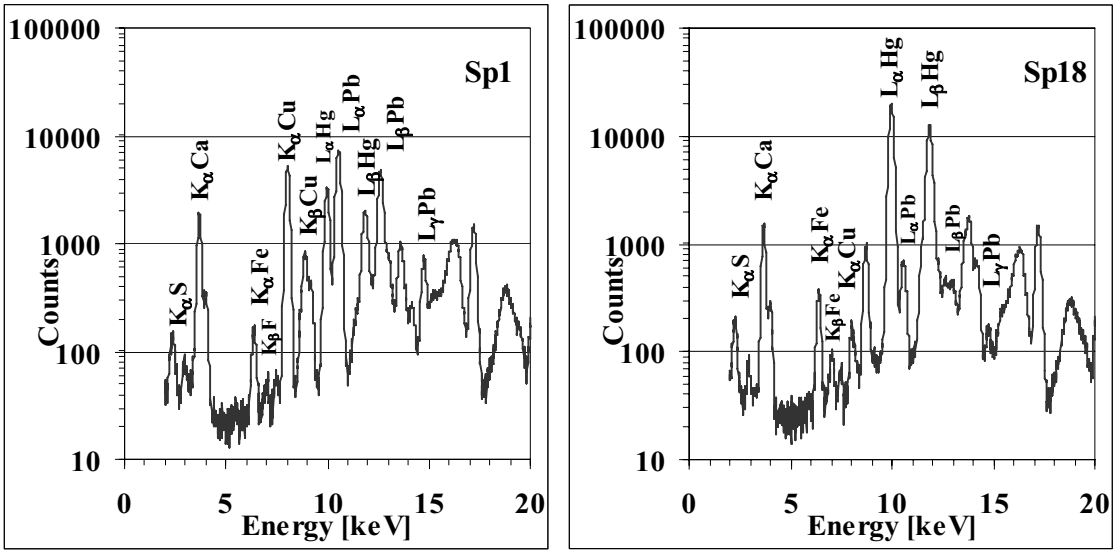

Figure 1: Fresco of the Virgin Mary with Child at Žirovnice Castle. Spectrum Sp1-small angle, green pigment, Spectrum Sp18-mantle of kneeling figure, red pigment

The mediaeval fresco of St. Hieronymus was discovered in the Church of Our Lady before Týn behind a Baroque side altar. This fresco was unique not only for its preserved state, but also for the techniques used: It was a classical fresco painted without organic materials. This type of the fresco is very rare in the Bohemia region. The investigation confirmed pigments commonly used in this period: Iron Oxide Reds and Red Ochres, Azurite, Malachite and Lead White.

At Karlštejn Castle our task was to date particular parts of the frescos restored in the 19th century, during the reconstruction of the castle. An analysis of the XRF spectra of the pigments is able to provide information about the type of pigments. The 14th century painters used different types of pigments than painters in the 19th century, and the application of XRFA enables us to differentiate the mediaeval and new parts of the fresco.

The red and black pigment was used as a marker of the mediaeval part of the fresco, see Fig. 2. The red pigment used in the 14th century was a mixture of Vermilion, Saturn Red, and Red Ochres. Red Ochres with Chinese White were used as a red pigment in the 19th century. An admixture of Mars Black with Saturn Red and Verdigris was used for tinting the black pigment in the 14th century. This pigment differs from the black pigment used in the 19th century (Mars Black with traces of Zn) [2].

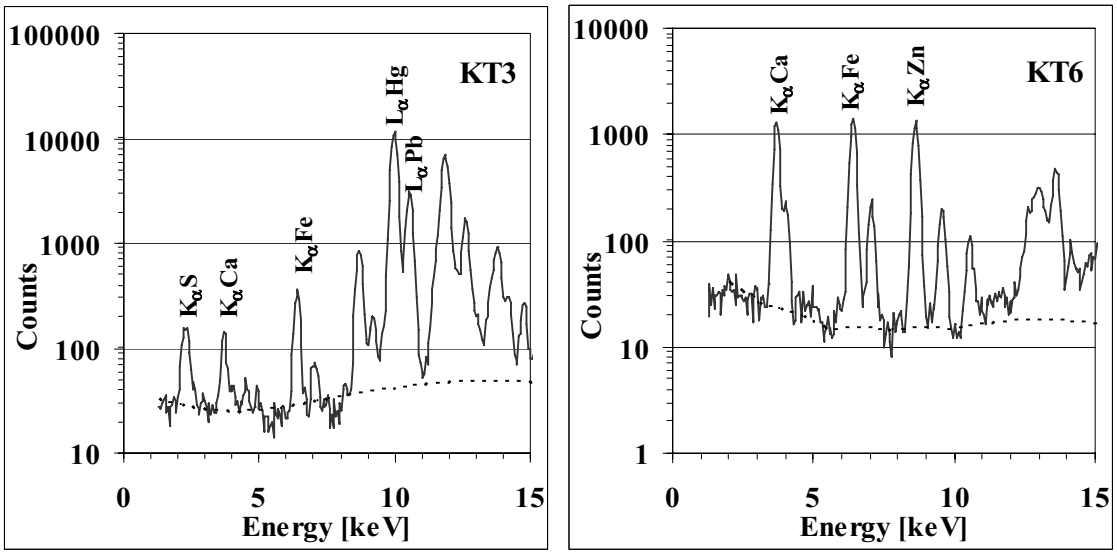

Figure 2: XRF spectrum of the red pigments in the fresco. At Karlstejn Castle, the red pigment used in the 14th century was a mixture of Vermilion, Saturn Red and Red Ochres. Red Ochres with Chinese White were used as a red pigment in the 19th century

Conclusion

The richness of the fresco paintings in the Bohemian region is remarkable. Analyses of the pigments used by artists in the past can provide a great deal of new information as more investigations are made. Better knowledge of this heritage is very desirable and can also help to find mutual influences with other European regions.

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Deterioration factors of Coptic wall paintings in Al Qurna and Wadi El Natrun-Egypt

Moussa (1), B. Christaras (2), J. Stratis (3), M. Ali (1)

(1) Conservation Department-Faculty of Archaeology-Cairo University-Egypt, moussa@geo.auth.gr
(2) Department of Geology-Aristotle University of Thessaloniki- Greece, christar@geo.auth.gr
(3) Department Of Chemistry-Aristotle University of Thessaloniki-Greece, jstratis@chem.auth.gr

- Wadi El-Natrun is a sandy depression located west of the Nile delta, latitude 30°17' and 30°38'N, longitude 30°02' and 30°30'E.
- It is directed NW-SE, about 72 feet under sea level, while Al Qurna is located at the Nile's west bank of Thebes about 25.67°N 32.70°E.
- Its height is about 88m / 288 feet above sea level. Wall paintings in both areas which have two different geological structures are affected by two different climatic conditions -Mediterranean and desert- which were studied analytically following their effect (Figs. 1, 2).
- Temperature and Relative Humidity registering showed a great variation in climatic conditions at the two areas between day and night, summer and winter.
- Rock, stone mortar and pigment analysis were achieved by means of non-destructive methods, chemically and microscopically (Fig. 3). Micro XRF, XRD, scanning electron microscope analysis showed that Copts continued to use the same pigment materials of ancient pharaohs, red pigment is hematite, yellow is goethite, blue is Egyptian blue, green is cerossite, black is mixed of carbon and magnetite, white is gypsum and brown pigment is hematite of Aswan, (Fig. 4).
- As conditions are suitable for microbial growth; bio-deterioration was studied separately, *Aspergillus glaucus* represents the most dominant fungal flora in Wadi El Natrun, while *Aspergillus fumigatus* represents the most dominant fungal flora in Al Qurna (Fig. 5) man made deterioration is one of the effective factors which were studied.
- A conservation plan was put to preserve the Coptic wall paintings in the studied areas.


Fig. 1


Fig. 2


Fig. 3

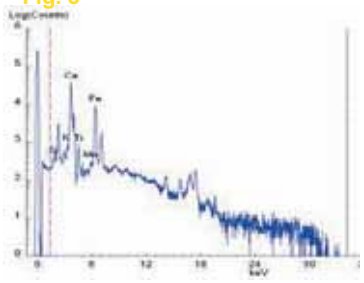
Fig. 4. Mmicro XRF diagram of red pigment Al Qurna

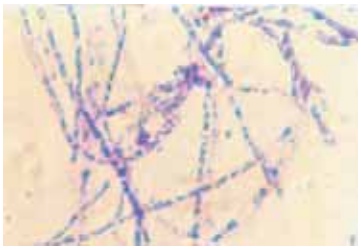
Fig. 5. *Aspergillus glaucus* under microscope-Wadi El Natrun

Deterioration factors of Coptic wall paintings in Al Qurna and Wadi El Natrun-Egypt

A. Moussa[1], B. Christaras[2], J. Stratis[3] and M. Ali[1]

[1] Conservation Department - Faculty of Archaeology - Cairo University-Egypt
[2] Department of Geology, Faculty of Science, Aristotle University of Thessaloniki, Greece
[3] Department of Chemistry, Faculty of Science, Aristotle University of Thessaloniki, Greece

Wadi El-Natrun is a sandy depression located west of the Nile delta, latitude 30°17' and 30°38'N, longitude 30°02' and 30°30'E. It is directed NW-SE, about 72 feet under sea level, while Al Qurna is located at the Nile's west bank of Thebes about 25.67°N 32.70°E. Its height is about 88 m / 288 feet above sea level. Wall paintings in both areas which have two different geological structures are affected by two different climatic conditions – Mediterranean and desert – which were studied analytically following their effect. Temperature and Relative Humidity registering showed a great variation in climatic conditions at the two areas between day and night, summer and winter. Rock, stone mortar and pigment analysis were achieved by means of non-destructive methods, chemically and microscopically. Micro XRF, XRD, scanning electron microscope analysis showed that Copts continued to use the same pigment materials of ancient pharaohs, red pigment is hematite, yellow is goethite, blue is Egyptian blue, green is cerossite, black is mixed of carbon and magnetite, white is gypsum and brown pigment is hematite of Aswan, figure (1). As conditions are suitable for microbial growth; bio-deterioration was studied separately, *Aspergillus glaucus* represents the most dominant fungal flora in Wadi El Natrun, while *Aspergillus fumigatus* represents the most dominant fungal flora in Al Qurna, figure (2) man made deterioration is one of the effective factors which were studied. An applicable plan for conservation was put to preserve the Coptic wall paintings in the studied areas.

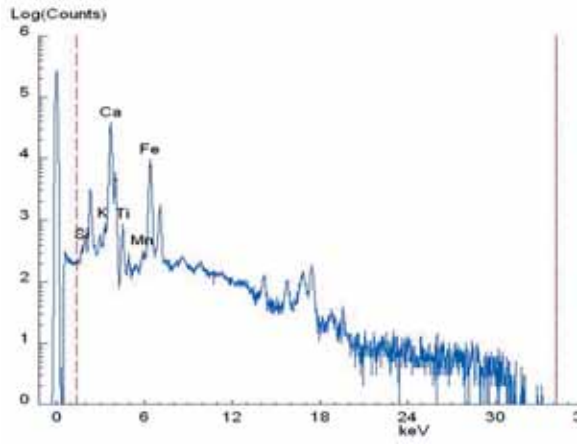

Figure 1: Micro XRF diagram of red pigment Al Qurna

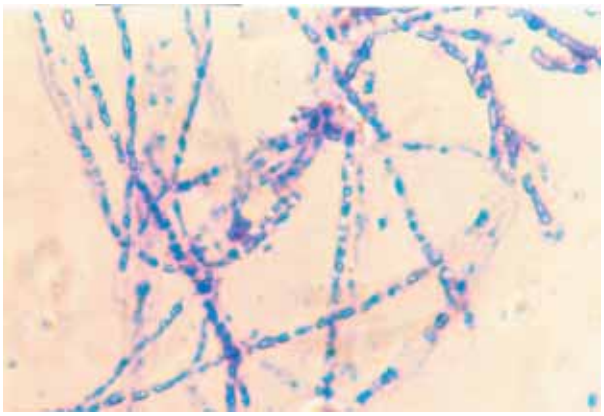

Figure 2: Aspergillus glaucus under microscope-Wadi El Natrun

FRAGMENTARY MURAL PAINTINGS – POSSIBILITIES OF AESTHETIC PRESENTATION AND EXEMPLARY COMMUNICATION

Stephanie Fundel (1), Mona Hess (1), Rainer Drewello (1) and Monica Mayer (2)

(1) Otto-Friedrich-University of Bamberg, Institute of Archaeology, Building Archaeology and Heritage Conservation (IABD), Germany

(2) Otto-Friedrich-University of Bamberg, Institute for Theoretical Psychology, Germany

stephanie.fundel@ggeo.uni-bamberg.de **Phone: + 49(0)951-863-2470;** rainer.drewello@ggeo.uni-bamberg.de **Phone: + 49(0)951-863-1133**

mona.hess@ggeo.uni-bamberg.de **Phone: + 49(0)951-863-2470;** monica.mayer@ppp.uni-bamberg.de **Phone: + 49(0)951-863-1956**

ABSTRACT

The former Dominican Church in the City of Bamberg, a UNESCO World Heritage Site, possesses a versatile collection of mural paintings of high artistic quality, primarily dated to the 14th to 16th century.

Since January 2005 there is a research project in the Dominican Church in Bamberg, supervised by Prof. Rainer Drewello, Institute of Archaeology, Building Archaeology and Heritage Conservation (IABD) of University Bamberg. For the project an area was selected, which shows the specific problems of superimposed mural paintings. The area consists of three high quality drawings referred to different phases of decoration. In course of the centuries new pictures were placed on top of existing ones.

Due to the insufficient removal in the 20th century and decades of persistent neglected maintenance the mural paintings suffered by an amount of different damages.

Now, countless fragments of layers of paintings cause a confusing appearance and bad legibility of the medieval artworks. The Department of Conservation Science, the Laboratory for Semantic Information Technology and the Institute for Theoretical Psychology are three institutions of Bamberg University closely cooperating in the development of concepts and software for supporting professional work in conservation science as well as its intelligent presentation to the public. In the context of the research project two software components, the *Digitales Gebäudearchiv (DGA)* and the *Mobile Mapping System (MMS)*, were used.

The main focus of the research project is the aesthetical treatment of the superimposed and highly degraded wall paintings. Virtual simulations are useful to discuss the various possibilities of restoration and preservation treatments without injuring the original. Furthermore, the mappings are predestine to become the basis for increasing the accessibility and legibility of the depicted works of art.

Fig. 1: Dominican Church, mural Paintings (IABD, 2005)

Fig. 2: fragmentary murals (IABD, 2005)

Fig. 3: mobile mapping (Leicht, 2005)

CONTENTS

- Art historical and technological examinations.
- Documentation by a novel mapping tool, the *Mobile Mapping System (MMS).*
- Achiving of data by the *Digitales Gebäudearchiv* (*DGA*).
- Virtual discussion of possible aesthetic interventions; conservation and preservation of the murals.
- Psychological profiling of the visitors.
- Communication of the contents.

DIGITAL BUILDING ARCHIVE AND MOBILE MAPPING SYSTEM [1]

The large amount of data was to be archived systematically. For this, digital software specialised in the space-oriented filing of information, the so-called *Digitales Gebäudearchiv (Digital Building Archive, DGA)*, is employed. The *DGA* is a documentation and information system which is charged with the administration of data concerning architectural structures. It is divided into a data administration unit, the "*Digital Archive*" (*DGA*) and a data acquisition module, the *Mobile Mapping System.* The hierarchical order of the respective historic building is freely definable. Navigation through the archive is carried out via the conventional tree structure - or via the building's constructional drawing. Documents to be archived can be assigned to specific parts of the building and provided with meta-data. The transfer of data from existing systems is carried out using "drag&drop" functions: the associated meta-data are automatically registered in the process. This component of the system was developed by the University of Passau under the direction of Prof. Freitag at the Institut für Informationssysteme und Softwaretechnik (IFIS).

The paintings were documented using a novel mapping tool, the so-called *Mobile Mapping System* (*MMS*). *MMS* was developed under the direction of Prof. Schlieder of Bamberg University's Chair for Computing in the Cultural Sciences.

The documentation tool supports the semantic search within the *DGA*, generates the meta-data important for documentary purposes and turns the software into a fully-fledged documentation and archiving solution with option for the integral search for space-related data. Since the real architecture offers access to the digital information, the system solution bears normative character for typologies and terminologies. The *DGA* can also be adapted to various languages through use of language masks. In addition, an analysis of damage development (monitoring) is possible after the cartographic documentation with the *MMS* mapping software. Using the CAD-based software, graphic and content information can be linked and archived in a database via a mobile computer (tablet PC).

Fig. 4: Structure of the MMS (Fundel, 2005).

Fig. 5: Structure of the DGA (Hess, 2005).

AESTHETIC PRESENTATION AND PSYCHOLOGICAL INVESTIGATIONS

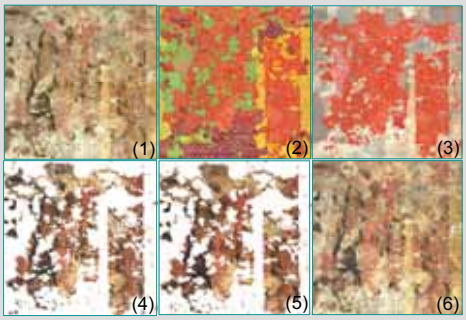

Fig. 6: Process of planning an aesthetical intervention; (1) high-resolution picture; (2) and (3) *MMS*-mapping; (4) separation of one phase; (5) virtual retouching; (6) combination of (1) and (4) for planning a restoration

On the basis of the *MMS*-mapping, we can demonstrate the different phases of painting separately. Through the separation of single phases of painting the effects of aesthetic interventions on the appearance of the murals can be simulated in a subsequent step. This serves as an instrument in planning on the one hand; on the other, the separation serves as an important aid to the visitors to understanding and clarifying the complex inventory of paintings.

A particular emphasis of the project is the communication of the contents of the medieval paintings. For this, the visitors of the Dominican Church are interviewed with psychological assistance about their personal perception of the fragmentary chaos of paintings. The Institute for Theoretical Psychology at Bamberg University is investigating the mental processes (motivation, cognition, emotion) occurring in the perception of fragmentary art based on model considerations [2]. Furthermore, it is to be investigated to which operations in data processing aesthetic perception can be ascribed.

The first results of the psychological examinations afford a detailed insight into the mental processes at work in the perception and communication of the Dominican Church's murals. Based on these analyses, profiles of the visitors are assembled. The conservation scientists compile and present information aligned to suit the profiles.

This interdisciplinary strategy affords the possibility of illuminating a destroyed work of art holistically, which represents a new and exemplary approach to the treatment of badly conserved works of art.

ACKNOWLEDGEMENTS

We wish to express our gratitude to the Messerschmitt Foundation Munich, the Bamberg Symphony Orchestra, and the Otto-Friedrich-University Bamberg for their support of this research project.

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Fragmentary mural paintings – possibilities of aesthetic presentation and exemplary communication

S. Fundel[1], M. Hess[1], R. Drewello[1] and M. Mayer[2]

[1] Otto-Friedrich-University Bamberg, Institute of Archaeology, Building Archaeology and Heritage Conservation, Germany
[2] Otto-Friedrich-University Bamberg, Institute for Theoretical Psychology, Germany

Keywords: fragmentary mural paintings, Mobile Mapping System, Digitales Gebäudearchiv

Introduction and content

In order to maintain public interest in our cultural heritage, appreciation of the material objects of the past must not be lost. That which is appreciated and thought to be of value will be conserved. But conservation measures are often controversial with the question at the centre of debate often being not *whether,* but rather *how* they are to be implemented. Should one conserve puristically and maintain only that which still exists? Or should one take a further step and display through restoration that which is almost entirely lost? The latter aims at restoring dignity to lost contents and at making them tangible for the viewer. This comes with certain dangers, since for the most part it is possible to choose only one of a number of very different alternatives. In the field of heritage conservation one often encounters fragmentary works of art which prove inaccessible to most viewers precisely because of their defects. This is exactly the problem presenting itself in Bamberg's Dominican Church which features a complex inventory of superposed murals of high artistic quality. The individual pictorial programmes from the early 14th to the closing 16th century can no longer be deciphered due to their fragmentary nature, especially as the contents are hardly anchored in contemporary consciousness. It was decided by Prof. Rainer Drewello in 2005 to institute a research team of restorers, architects, computer scientists, and psychologists to solve the problem of how to deal with the chaos on the walls of the present university auditorium. The bizarre fragmentary nature of the murals was to be preserved, and at the same time the beholder was to be motivated to discover their contents. This necessitated a new approach to research. Accordingly, the aims of the interdisciplinary project are varied. The campaign began with a complementary art historical and art technological examination of a selected area of the murals. The paintings were documented using a novel mapping tool, the so-called *Mobile Mapping System* (*MMS*) [1]. Subsequently, the possible aesthetic interventions were simulated by means of a virtual discussion of alternatives prior to actual conservation and restoration. In parallel, the large amount of data already existing and still growing was to be archived systematically. For this, digital software specialised in the space-oriented filing of information, the so-called *Digitales Gebäudearchiv (Digital Building Archive, DGA)*, is employed. A particular emphasis of the project is the communication of the contents of the medieval paintings which are difficult to grasp. For this purpose very differently educated visitors of the Dominican Church are interviewed with psychological assistance about their personal perception of the fragmentary chaos of paintings. We are aiming at an exploration of the destroyed work of art which turns looking at the painting into an intellectual pleasure and which whets the appreciation for the conservation of our cultural heritage.

European dimension

The overall impact of a work of art is significantly altered through conservation and restoration, as any intervention is associated with the desire to improve the aesthetic appearance. The measures are contingent upon personal opinions and current tastes and significantly alter the perception of a work of art. Today, restoration is predicated on the artistic and historical

statement of the work interpreted as source. Consideration is given simultaneously to both the authenticity and the aesthetic qualities. In the case of fragmentary works of art it is always necessary to consider a certain degree of reconstructive interventions. Virtual reconstruction and retouching could be used in hypothetical representations of that which is to be shown, and also to plan ahead for the actual intervention. But in the past they hardly were used, not least because every virtual discussion presupposes a prior examination which costs money. But it seems to us that virtually playing with the possibilities is one of the preconditions for a responsible treatment of our cultural heritage which is worth its money. In recent years, there has been a noticeable trend towards software supported working procedures and towards the use of digital documents in the conservation of architectural heritage. In the context of the research project two software components, the *DGA* and the *MMS*, were used. In conjunction, they form a novel multifunctional documentation and information system, which is already in use across Europe. At the moment there exist great deficits in the communication and public relations work of restoration projects and in the communication of fragmentary art. Complex decisions for or against specific measures in particular are mostly made by a small circle of experts. The public – the actual addressee – is excluded as a rule; this is a mistake if one wishes to strengthen the general consciousness of the value of our cultural heritage and the power of democratic decisions. At the very least, the viewing conventions and the stimulating psychological processes at work precisely in the perception of fragmentary and destroyed works of art should be taken seriously and the viewer should be allowed to take part in the intellectual game. For without active looking the trend towards indifference and ignorance will grow, which cannot be in the interest of a Europe defining itself not least by its cultural values.

Innovation and originality

It is the concern of the research project to unify the various results accruing over the course of the conservation and restoration of fragmentary art into an exemplary solution for the collection and archiving of computer file formats as well as for the subsequent targeted preparation of the collected insights for the public. To this end the following are employed among other aids: the Digitales Gebäudearchiv is a multifunctional documentation and information system which is charged with the administration of data concerning architectural structures. The DGA represents a new methodic dimension in documentation and archiving. It is divided into a data administration unit, the “Digital Archive” (DGA) and a data acquisition module, the MMS, in which the definition of the inventory system is space-oriented. The freely definable hierarchical order of the respective historic building is a novelty. Navigation through the archive is carried out via the conventional tree structure - or via the building’s constructional drawing. Documents to be archived can be assigned to specific parts of the building and provided with meta-data. The transfer of data from existing systems is carried out using “drag & drop” functions: the associated meta-data are automatically registered in the process. This component of the system was developed by the University of Passau under the direction of Prof. Burkhard Freitag at the Institut für Informationssysteme und Softwaretechnik (IFIS). The mapping tool *MMS* was devised for mobile terminals under the direction of Prof. Christoph Schlieder of Bamberg University’s Chair for Computing in the Cultural Sciences for this purpose. The documentation tool supports the semantic search within the *DGA*, generates the meta-data important for documentary purposes and turns the software into a fully-fledged documentation and archiving solution with the option for the integral search for space-related data. Since the real architecture offers access to the digital information, the system solution bears normative character: debates of nomenclature due to differing typologies or terminologies of buildings are overcome through the use of the “language” of drawings. The *DGA* can also be adapted to various languages through use of language masks. It is recommended for the use as archiving tool for all site offices by the Europäische Dombaumeistervereinigung (European association of cathedral restorers) [2] and thus could become a platform for a large circle of users, building bridges throughout our polyglot Europe. In addition, an analysis of damage development (monitoring) is possible after the cartographic documentation with the *MMS* mapping software. Using the

CAD-based software, graphic and content information can be linked and archived in a database via a mobile computer (tablet PC). In the meantime, the software is being put to use in several European countries. The Institute for Theoretical Psychology at Bamberg University is investigating the mental processes occurring in the perception of fragmentary art based on model considerations [3]. Evidently, the theory is capable of explaining and predicting complex behaviour and its effects on cognition, emotion, and motivation. Furthermore, it is to be investigated to which operations in data processing aesthetic perception can be ascribed.

Impacts

All accruing data of the examinations, conservation, and restoration of the Bamberg Dominican Church's mural paintings are systematically archived with the aid of the *DGA*. Widely differing data formats can be specifically and quickly recalled as needed. Mapping the mural paintings with *MMS* delivers a documentation densely packed with information on both the state of conservation of the paintings and the implemented measures. On the basis of the *MMS* inventory mapping, we can demonstrate the different phases of painting separately. Through the separation of single phases of painting the effects of possible aesthetic interventions on the appearance of the murals can be simulated in a virtual debate of alternatives in a subsequent step. The intervention in the object can be concretely planned on the PC in advance. This serves conservation scientists as an instrument in planning on the one hand; on the other, the separation serves as an important aid to the Dominican Church's visitors to understanding and clarifying the complex inventory of the mural paintings. The decision making process in favour of a particular variant of restoration becomes comprehensible to the general public. This represents a novel approach to solving the complicated restoration of fragmentary art. Consequently, the virtual discussion of alternatives serves as an aid to planning and deciding on the restoration of fragmentary works of art. The public is informed about and sensitised to the conservation and restoration measures. The first results of the psychological examinations afford a detailed insight into the mental processes at work in the perception and communication of the Dominican Church's mural paintings. Based on these analyses, profiles of the visitors are assembled. The conservation scientists compile and present information aligned to suit the profiles. This interdisciplinary strategy affords, for the first time, the possibility of illuminating a destroyed work of art holistically, which represents a new and exemplary approach to the treatment of badly conserved works of art.

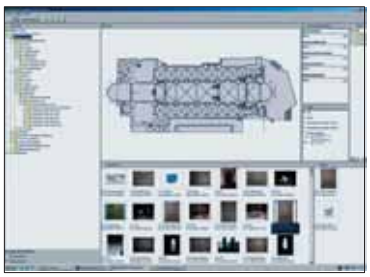

Figure 1: Structure of the DGA (Hess, 2005)

Figure 2: Structure of the MMS (Fundel, 2005)

Acknowledgement

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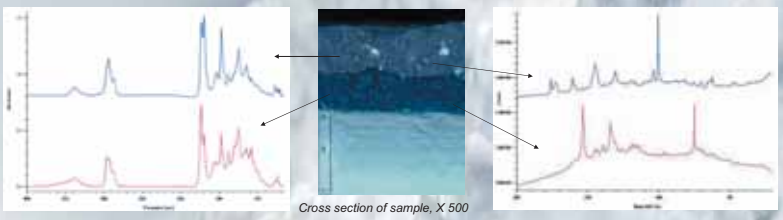
[3] Dörner, Dietrich 2001, *Bauplan für eine Seele*, Rowohlt, Reinbeck bei Hamburg.

CHARACTERIZATION, AGEING AND AUTHENTIFICATION OF WORKS OF ART: POLYURETHANE PAINTS AND FOAMS

Colombini A.[1], Leal Romero V.[1], Lamothe V.[2], Soumireu-Lartigue S.[2], Antoine J.[2]
[1] Laboratoire du Centre Interrégional de Conservation et Restauration du Patrimoine (C.I.C.R.P.). France
[2] Laboratoire de la Police Scientifique de Marseille. France

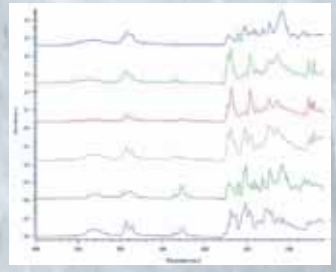
Polyurethanes have appeared lately in works of art even though polyurethane elastomers have been used since the mid XXth century. The alterations of modern materials, and more specifically, those which used polyurethane in the 1960's, have already become one of the major issues of conservation treatments. Therefore, it is important to characterize and study the behaviour of these polymers in order to provide a better understanding of both the ageing and the interaction with other materials. The authentification is equally a critical question in criminalistic investigations as well as, in the expertise of works of art. The aim of this study is to introduce a joint approach in the knowledge of these polymers.

Characterization



Cross section of sample, X 500

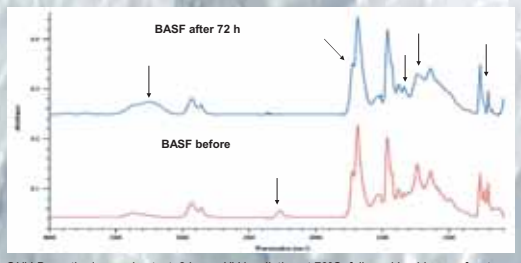
FTIR (left) and Raman (right) spectra of an Amiral blue Citröen C4 sample, recorded from a cross section of blue basecoat and translucent clearcoat; the thick white polypropylene base was not analysed. FTIR spectra of the different coats are very similar making their characterization difficult. The differentiation between clearcoat and solidcoat can be achieved by Raman microscopy.



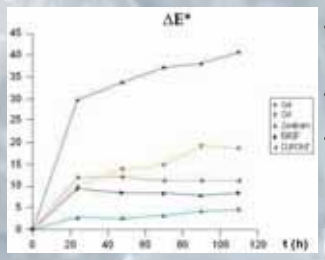
Foam HR-AT, Soloplast
Zenitram, DUPONT
JF110405, BASF
9219456, DUPONT
G4, Soloplast
G8, Soloplast

FTIR spectroscopy of polyol polyether (Foam HR-AT), polyurethane-acrylate (Zenitram), polyol polyester (BASF, DUPONT), polyol polyether (G4), polyol polyester (G8)

Wheathering accelerated ageing



QUV-B weathering ageing test: 8 hours UV irradiation at 70°C, followed by 4 hours of water condensation at 50°C in the dark; irradiance 0.71 W/m²/nm, samples applied on linen canvas.



- The highest colour changes occured with the polyol polyether G4 while polyol polyester (BASF) is more resistant
- Aliphatic isocyanate (G8) showed a better colour stability than aromatic isocyanate (G4)
- The polyurethane-acrylate (Zenitram) remains the most resistant to degradation

Colour change with handheld HunterLab spectrocolorimeter: Miniscan XE Plus diffuse mode D65/10°, viewing area 4mm

FTIR spectra of polyol polyester BASF before and after wet cycle QUV-B exposure.

- Decrease of the IR absorbance at:
  1720 cm^{-1} (C=O stretching free urethane), 1300 cm^{-1} (C-H scissoring in aromatic ring, C-N stretching), 1234 cm^{-1} (ester C-O-C stretching) and 730 cm^{-1}
- Increase of the IR absorbance at:
  3251 cm^{-1} H-bonded OH or NH, which can be considered as an oxidation product
- The disappearence of the IR absorbance at:
  2256 cm^{-1} out of phase N=C=O stretching isocyanate residual functional group

• Results have brought to the fore, the complementarity of Raman technique, which is more suitable in the identification of both colouring matters and binders, and FTIR, better appropriated for studying the chemical changes.

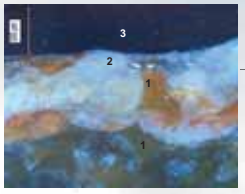
• The difficulty in correlating the research with the analysis of materials found in the XXth century, is partly due to the manufacturing process. Nevertheless, it allows us to benefit from the manufacturers knowledge and concern of durability and resistance of polymers.

• This study represents the first step in developing a relationship between laboratories with two different concerns. By joining knowledge of identification of polyurethane and behaviour of these materials in the ageing process, it would improve the understanding and the accuracy of analysis.

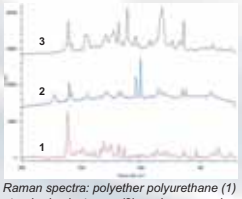
• Sophisticated and expensive analytical techniques can be shared between cultural heritage and forensic laboratories.

Case study

Cesar's sculpture "Expansion Controlée" 1967, 155 x 110 x 60 cm, 40 kg. First a polystyrene core of the structure is coated by several polyurethane running layers. Then, it is fully covered with a thick tinted epoxy paint.



Cross section of sample, X 200



Raman spectra: polyether polyurethane (1) standard polystyrene (2), and epoxy resin of the surface layer covering the foam (3)

Raman analysis revealed the presence of a mixture of polyether polyurethane with a polystyrene foam. Including an expandable polystyrene in the polyurethane reaction mixture reduces the cost of the manufactured foam. A side benefit of this, is that the resultant foam is less dense and has a better crush resistance. One may assume that Cesar was aware of these two aspects.

L.P.S

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Belle de Mai

7TH EUROPEAN COMMISSION CONFERENCE "SAUVEUR" SAFEGUARDED CULTURAL HERITAGE: UNDERSTANDING & VIABILITY FOR THE ENLARGED EUROPE. PRAGUE 31ST MAY - 3RD JUNE 2006

Contacts: **alain.colombini@cicrp.fr; vicente.leal@cicrp.fr**

Characterization, ageing and authentification of contemporary works of art: polyurethane paints and foams

A. Colombini[1], V. Leal Romero[2], V. Lamothe[3], S. Soumireu-Lartigue[3] and J. Antoine[3]

[1] Laboratoire du Centre Interrégional de Conservation et Restauration du Patrimoine (C.I.C.R.P.), France
[2] Master in chemistry, CICRP, France
[3] Laboratoire de Police Scientifique de Marseille, France

Key words: polyurethane, contemporary art, forensic laboratory, accelerated ageing, Raman spectroscopy

Introduction and content

Polyurethane paint only appears today in public collections even though polyurethane elastomer have been used since mid 20th century. Therefore, it is important to characterize and to study the behaviour of these materials since they are already becoming one of the major concerns of the conservation of the 21st century works of art. For this reason, it is necessary to rest on scientific skills in the field of synthetic resins like those of the forensic laboratories. The alterations of modern materials and more specifically, those which used polyurethane in the 1960's, have already become one of the major issues in conservation treatments. For example, the making of polyurethane foam sculptures, which was often empirical when first used, along with the instability of these polymers, makes the treatment of these objects very difficult [1].

Nowadays the term "polyurethane" is no longer a synonym of degradation especially when used as a paint medium. Indeed, the manufacture of the polymer has improved, the latter is really appreciated because of its durability, its colour fastness and its resistance to high temperatures, which for example, confers its wide use in the car paint industry. Even though, polyurethane paint has appeared lately in public collections, it is important to characterize and study the behaviour of these polymers in order to provide a better understanding of both the ageing and the interaction with other materials found in works of art. The complexity of implementing a conservation treatment method of this polymer is, that such versatile material can behave differently depending on the type of polyurethane elastomer used.

Polyurethane elastomers are formed when a (di- or poly) isocyanate and a polyol react in the presence of catalysts and additives. The nature of polyurethane produced varies according to the types of isocyanates and the polyols used. They are either polyester based or polyether based polyols. Even though they are both subject to degradation, mainly mechanical property loss, discoloration and hazardous chemical products release, such as, volatile organic acids, the polyester polyurethane is known to be more resistant to hydrolysis [2].

This programme is simultaneously run in the laboratory of the CICRP and in the forensic laboratory of Marseille. The first works rely on the understanding of the various alteration phenomena of paints containing polyurethane medium and on the techniques of characterization of polyurethane mainly found on bumpers. This work has been focused on the photochemical accelerated ageing test under UV-B light applied on experimental laboratory canvas samples, on colour measurement, and on the physico-chemical characterization of materials during the ageing process with the help of Raman and FTIR microscopy [3]. These also allowed to deepen the method of identification of polyurethane paint notably by FTIR microscopy in transmission mode and sample preparation for Raman microscopy.

Results have brought to the fore the complementarity of Raman technique, which is more performant in the identification of colouring matters and FTIR, better appropriated for studying the chemical change of materials, mainly resins [4].

European dimension

The authentification is equally a critical question in the criminalistic investigation as well as in the expertise of works of art. The aim of this study is to introduce a joint approach in the knowledge of these materials.

A community of European forensic laboratories has already implemented a European database of polymer paint that can be found in cars and thereby, optimising the scientific investigations of car paints. The aim of this approach is to homogenise FTIR spectroscopic method of identification. As result of this, it gathers data obtained from the car paint manufacturers and therefore, improves the reliability and the quality of results. The making and the materials used by artist are usually well documented. The difficulty in correlating the research with the analysis of materials found in the XX^{th} century works of art is partly due to, in the case of polymers, the manufacturing process. Nevertheless, it allows us to benefit from the manufacturers knowledge and concern of durability and resistance of polymers.

Innovative and originality

The study of the weathering accelerated ageing test of polyurethane binder has shown that photo degradation occurs rapidly. After 100 hours of ageing, the surface of the polyurethane test samples, containing no pigments, showed some yellow discolouration. These changes in appearance were correlated with the chemical modifications found with FTIR analysis. Although the photochemical instability of the polymer is well known, it is important to take into account that polyurethane was used without stabilizer and plasticizer additives. Since polyurethane foams have a significant amount of aromatic content, UV stabilizers are added to slow down the yellowing of foams upon exposure to light [5].

The UVB fluorescent lamps emit more damageable UV radiation (315 nm) where photo degradation is at its highest. These severe ageing conditions were purposely used, as this can be related to stressful environment surrounding works of art, in particular polyurethane painted foam sculpture exhibited in public places [6].

Criminalistic investigations do not take into account the ageing process of the materials identified. As this aspect is of prime concern in the conservation of works of art, the junction of the two approaches leads to a broader knowledge of these particular polymers.

Impacts

The results represents the first step of developing a relationship between laboratories with two different concerns. Even though each section has its own method of investigation, by joining knowledge of identification of polyurethane and behaviour of these materials in the ageing process, it would improve the understanding and the accuracy of analysis.

Sophisticated and expensive analytical techniques can be shared between cultural heritage and forensic laboratories. Raman spectroscopy has particularly demonstrated that sample preparation technique used is as an important tool for identifying both the colouring matter and the polyurethane medium [7].

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COST ACTION G8
NON-DESTRUCTIVE ANALYSIS AND TESTING OF MUSEUM OBJECTS: AN OVERVIEW OF 5 YEARS OF RESEARCH

Annemie Adriaens
Department of Analytical Chemistry, Ghent University, Belgium

Objectives

Achieve a better preservation and conservation of our cultural heritage

- by increasing the knowledge in museum objects through non-destructive analysis and testing
- by improving the synergy between art historians, archaeologists, conservators and analytical scientists

Benefits

- provide easy access to research equipment
- provide education and training possibilities
- expand collaboration networks
- enhance the capability of answering questions that remain unanswered in the field

List of member countries

AT, BE, BG, CH, CZ, CY, DE, DK, ES, FI, FR, GR, HU IL, IT, MK, MT, PL, PT, NL, RO, SI, SK, UK

COST Action G8 activities

- short term scientific missions
  - stay in laboratory of another member country
- working groups
  - coordinate research in specific fields
- workshops
  - exchange knowledge in broader group
- training schools
  - disseminate knowledge to newcomers

Working groups

- technology and authentication
- origin and provenance
- degradation processes
- preservation and conservation
- development of analysis procedures
- biological and material culture of Qumran at the Dead Sea

http://srs.dl.ac.uk/arch/cost-g8/index.htm

- aims and objectives of the action
- contact details of national representatives in the MC
- database of members of a special interest group
- objectives and membership of working groups
- information on working group meetings and work shops
- other relevant links related to G8 activities

Workshops

- Sep 2001, Genoa
  Non-destructive analyses in the conservation / restoration of museum objects
- Jan 2002, Ghent
  Development of analysis methods
- May 2002, Edinburgh
  Conservation Science 2002
- Jan 2004, Malta
  Benefits of non-destructive analytical techniques for conservation
- Jun 2004, Ljubljana
  Archaeometry with IBA and related methods
- Oct 2004, Zurich
  Inter-disciplinarity in non-destructive testing of museum objects
- Apr 2005, Bratislava
  In-situ non-destructive analysis and testing of museum objects
- Jun 2005, Seville
  Archaeometry with IBA and related methods

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COST Action G8: Non-destructive analysis and testing of museum objects: an overview of 5 years of research

Annemie Adriaens

Department of Analytical chemistry, Ghent University, Belgium

Key words: COST Action G8, non-destructive analysis, inorganic materials

Introduction and content

Europe has a particularly rich and diversified cultural heritage, including buildings, monuments and objects of all sizes, comprised of a great variety of materials. It forms the basis of our present and future cultures, and through the skills, beauty, and engineering genius it manifests, it is a vital source of inspiration and pleasure. Its exploitation, in the form of displayed objects, is a direct and indirect source of revenue through tourism and at the same time the basis for a rich diversity of learning. The conservation of the European cultural heritage is for these reasons a culturally important activity in its own right and an economic necessity.

Nevertheless the physical part of the European cultural heritage is deteriorating faster than it can be conserved, restored or studied. Assets are being lost, or at risk, through natural processes of decay (sometimes accelerated by poor environmental control), environmental disasters (sometimes exacerbated by human activity), the direct effects of enhanced public access (without commensurate conservation measures), conservation / preservation procedures whose long-term effects were and are not understood, and simple negligence.

The research required to alleviate this huge class of problems and at the same time progress the study of the European cultural heritage is interdisciplinary, needing the expertise of people directly involved with the cultural heritage (i.e. art historians, archaeologists, curators, conservators) as well as analytical scientists and other specialists at a basic research level.

The use of advanced analytical methods and techniques are an essential prerequisite in this field as they provide the means to understand the objects under investigation. Through the identification of materials and processes, we can reach back through time and develop a deeper understanding of the craftsmanship and technology that was used. Advanced analytical methods also allow us to perform authenticity studies or contribute to the development of simple diagnostic techniques necessary for practical applied conservation. The methods used in this field of research are identical with those used at the cutting edge of modern material science. Methods developed for advanced physics and chemistry, semiconductor and aerospace research and development, medicine and environmental research, have a commonality of application to both ancient and modern materials as problems encountered in both the advanced technology and cultural heritage areas are surprisingly similar. However, there is one essential difference – an art object or ancient artefact cannot be replaced, and the consumption or damaging of even a small part of it for analytical purposes must be undertaken only where the need is great. This leads either to the development, use and improvement of truly non-destructive techniques, which do not require a sample to be removed from the object, and which leave the object in the same state before and after analysis. In case where a sample must be removed, one should aim at the maximization of information, and the minimization of the consumed volume. This brings

us to the need for designed pathways which allow multi-instrument analytical approaches, including thought-through sample preparation schemes (removal from the object, preparation, and packaging for transport). Clearly established schemes lead to a better integration of activities and to an improvement of the representivity and the reproducibility of analytical results.

In the case of the non-destructive techniques, there is a further consideration – portability. It is often undesirable (or even impossible) to move an artefact to a laboratory where large scale analytical equipment is housed. Alternatively, it may be the environment of an object which requires monitoring in a non-invasive way (e.g. so as not to disrupt visitor experience).

European dimension

The concept of a "European Cultural Area" is also important as it creates a framework for all activities associated with cultural heritage and it highlights at the same time the multi-facetted character and variety of European cultural heritage. The few national programmes available no doubt are to be appreciated, but they only serve local needs, leading to a loss of strategic output, risk of duplication, and reduce the competitiveness of the research internationally. Therefore a European wide approach is essential. If too many projects are managed only at national level, their importance for Europe as a whole may be overlooked, and vital synergies missed [1].

Innovation and originality

The main objective of Action G8 (2000-2006) has been to increase the knowledge of museum objects through non-destructive analysis and testing, thereby trying to achieve better preservation and conservation methods for our cultural heritage [2-3]. Today many questions within this field still remain unanswered, not only because of the lack of exchange of knowledge and the difficulty in following-up collaborative initiatives in this multidisciplinary community, but also because several investigation techniques or treatments still need to be introduced or established. It is for these reasons that Action G8 seeks to create a European wide environment, in which people directly concerned with the maintenance of our cultural heritage and their colleagues in analytical science can exchange knowledge.

COST Action G8 has four main scientific activities. The first one includes organising short-term scientific missions between participating institutions. The goal of these missions (5 days – 2 months) involves the training of scientists of both professional groups in the other's field as well as the transfer of practical experience among European countries. Secondly, regular meetings in the form of workshops are organised, often in collaboration with museums and conservation institutes, to exchange obtained knowledge in a broader group, to discuss new themes, and to build interest and create possibilities for new collaborations. The achieved knowledge is further being disseminated via training schools. As a fourth activity, separate working groups have been created. The working groups allow a close collaboration and an extended and efficient exchange of knowledge within a specific topic, and therefore a more efficient way of publishing the obtained results. The following themes are addressed:

- Technology and authenticity, involving the identification of the materials and their production techniques. Within this working group two distinct but related topics are studied: (1) the investigation and verification of ancient recipes starting from the Mesopotamian and Egyptian texts up to the 19th century books of technology descriptions about how craftsmen prepared and made their products are available and (2) the authentication of art and archaeological objects, i.e. the identification of fakes.
- Origin and provenance, including the characterization and location of the natural sources of the raw materials used to make (museum) objects. The main goal is to contribute to establishing patterns of raw material procurement, trade or exchange.

- Degradation processes, corrosion, weathering. This working group deals with the problem of alteration of museum objects and the way non-destructive techniques can be used to measure this damage or monitor it with time.
- Preservation and conservation. The working group is concerned with the treatment of works of art in order to slow down deterioration, the identification of the nature and extent of damage, the assessment of the causes of deterioration. Work in this field also implies the control of the environment in which the object is located, such as monitoring of the temperature, relative humidity and lighting, ensuring proper storage, support and security.
- Development of analysis procedures involving three main goals: (1) the use and improvement of truly non-destructive techniques (they do not require a sample to be removed from the object), (2) the maximization of information and minimization of consumed volume where a sample must be removed and (3) the development of portable / mobile equipment so monitoring can be done on site.
- Biological and Material Culture of Qumran at the Dead Sea. This working group deals with three aspects of the study of material remains at Qumran, i.e. the biological and the material cultural ones and the conservation of this cultural heritage.

Impacts

The use of analytical techniques for cultural heritage applications is receiving an increasing amount of attention, both by analytical scientists as well as by people more directly involved with the preservation of our cultural heritage (e.g. art historians, curators, archaeologists, conservators, etc.). This is not only evidenced by the vast number of scientific papers published in the literature over the past few years, but also by the various conferences and workshops in the field. COST Action G8 has had a significant contribution here.

There is also no doubt that current research has strengthened the multidisciplinary community in this field. It has enhanced the capability for answering questions related to museum objects, which could not readily be solved, and the exchange of knowledge in both directions. Moreover Action G8 has provided museums and similar institutes easy access to universities and research facilities that have the required analytical techniques and related expertise available.

Acknowledgement

A special word of thanks to COST Action G8 and its members for a very fruitful and pleasant collaboration in the field of cultural heritage research.

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COST Action G7
Artworks Conservation by Laser

AN EXAMPLE OF SUSTAINABLE INNOVATION IN FULL DEVELOPMENT IN EUROPE

List of member countries

AT, BE, CY, DK, FI, FR, DE, GR, HU, IL, IT, LV, ML, NL, NO, PL, PT, RO, SI, ES, UK

Web site : http://alpha1.infim.ro/cost

Objectives

To promote research and validation of laser techniques in conservation in three main areas, organized in working groups:

- WG1 Laser systems and procedures for cleaning applications
- WG2 Laser and optical systems in analysis and diagnostics
- WG3 Real-time optical equipment for environmental aspects and response of artworks.

To foster interdisciplinary teams composed by scientists, art historians, archaeologists, conservators to exploit correctly the benefits of such innovative techniques and disseminate them worldwide to the conservation community.

Benefits

- Set-up of scientific approaches for experimentation and validation
- Exchange and comparison of results
- Improved comprehension and devising of new ideas
- Dissemination of best practices in the conservation community

Activity

14 Management Committee Meetings and Workshops organized in 6 years: Brussels, Bucharest, Vienna, Heraklion, Berlin, Helsinki, Florence, Lisbon, Nantes, Gdansk, Tulcea, Ljubljana, La Valletta.
COST G7 has also contributed to 13 international conferences and an exhibition (Ferrara 2003).

Results

- Data collection about literature, laser systems, future demands, validation cases.
- Promotion of experimentation of laser techniques by interdisciplinary teams in many projects and networks, leading to the following results :
- Acceptance of side effects-free laser cleaning of stone as best preservation method for ancient patinas on statues, monuments and facades.
- Acceptance of laser cleaning of metals (gilded bronze, silver, aluminum, iron, lead) as best preservation method for coatings, faint traces and details.
- Demonstration of laser cleaning of organic materials (paper, parchment, textiles) and inorganic materials (glass, ceramics, terracotta).
- Validation of structural diagnostics based on holographic interferometry.
- Validation of fresco's defects based on laser Doppler vibrometry.
- Validation of material analysis based on LIB Spectroscopy.
- Validation of 3D documentation based on laser scanning.
- Publication of an handbook for a safe use of lasers in conservation.
- Spread of restoration activity employing laser techniques for many important works of art and archaeological sites in Austria, Greece, Italy, France, United Kingdom, Germany, Holland, Sweden, Spain, Portugal, Romania, Poland, etc.

The G7 group

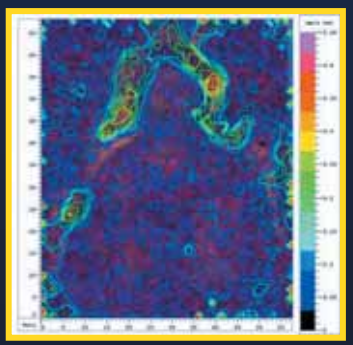
Management Committee Meeting in Lisbon

COST G7 stand at RESTAURO 2003 Exhibition in Ferrara

Laser cleaning of stone in Vienna, Paris, Athens, Madrid, Florence, Liverpool, Warsaw, Lisbon, etc.

Laser cleaning of gilded bronze in Florence

LIDAR monitoring at work in Lund and Florence



Icona's detachment detection in Athens and Ancona

Laser cleaning of paintings in Heraklion and Hengelo

Laser Techniques in Conservation after COST Action G7: an effective innovation available in Europe

Renzo Salimbeni

Institute of Applied Physics "Nello Carrara" of CNR, Italy
COST Action G7, Belgium

Key words: laser, conservation, innovation

Introduction and content

Laser techniques in conservation of cultural heritage have been experimented in Europe since more that thirty years [1]. After that many research projects organised at the European level have contributed to the development of advanced laser systems for diagnostics and cleaning, still the acceptance of these innovative methodologies has been growing very slowly for a long period of time [2]. The COST Action G7 "Artworks Conservation by Laser" has played its unique role of networking a vast interdisciplinary community of experts since the year 2000, with the main objective of promoting laser techniques for conservation by means of cooperative experimentation, by comparing the experiences and disseminating best practices.

The validation of these advanced cleaning techniques during COST Action G7 has been extensive and diffused in many European countries, especially for stone and metals. Laser-based diagnostics have also specialised their tasks toward material analysis, defects detection and multidimensional documentation. In many European countries national interdisciplinary networks could grow, managing the experimentation of these techniques and also a technology transfer to end-users. So doing the appreciation for these techniques has been growing in all the conservation institutions involved at national level, disseminating a positive evaluation about the benefits provided by laser techniques in conservation. Several laser systems became products for the activity of professional restorers and their increasing sales demonstrate a growing utilisation throughout all Europe.

European dimension

Up to 21 European countries (Fig. 1) are participating to the activity of COST G7, with 36 national delegates in the Management Committee of the Action. Laser physicists, laser engineers, chemists, biologists, architects, art historian, conservation experts, restoration experts have worked together with great effectiveness. All the information about the activity may be found at the web site: http://alpha1.infim.ro/cost.
The activity proceeds through various means:

1) The organisation of Management Committee, Technical meetings and Workshops to exchange experience, to foster cooperative projects, to disseminate best practices to local conservation communities, to present results in conferences and exhibitions;
2) By carrying out Task 1 Collection of bibliography, Task 2a Data base on laser cleaning systems, Task 2b Data base on laser and optical methods for analysis, diagnostics and monitoring, Task 3 New research proposals, Task 4 Validation case studies.

In the course of G7 activity 14 Management Committee Meetings have been organised in Bruxelles (2000), Bucharest (2000), Vienna (2001), Heraklion (2001), Berlin (2002), Helsinki (2002), Florence (2003), Lisbon (2003), Nantes (2004), Gdansk (2004), Tulcea (2005),

Ljubljana (2005) and La Valletta (2006). Thematic workshops were organised in association with them, dedicated to the aim of dissemination and meeting with the national community of conservators and professional restorers. The contribution to various conferences (LACONA, SPIE, ALT, CLEO, ICONO-LAT etc.) has been also part of the G7 dissemination plan, and the last Management Committee Meetings before the conclusion of the activity (2006) have been dedicated to meet with experts, representative of the conservation activity coming from candidates east-Europe countries, from former Yugoslavian countries and finally from Mediterranean countries in the last G7 conference, held in La Valletta, Malta, on the 23-25 March 2006.

Innovation and originality

The role of COST Action G7 as a network of experts has been realised in a very innovative way, with a widely interdisciplinary group of experts that could debate on the various focus of the Action with effectiveness, could devise the proper measures to achieve the objectives, could exploit the scientific competition turning it in a cooperative effort of exchanging knowledge. This doesn't happen frequently and has been the basis for a successful conclusion of the Action. Furthermore the Action lifetime of six years has allowed to carry out a vast program of dissemination consisting of the organisation of 13 workshops, the contribution to other 13 international conferences, several scientific publications including two books: Cleaning Safely with a Laser in Artworks Conservation, and Handbook on the Use of Lasers in Conservation and Conservation Science.

Impacts

The growth of interest and use of laser techniques in conservation rose considerably during the lifetime of COST Action G7. Two factors may be considered as important indicators of the growth of interest: the number of publications or presentations submitted to international conferences and the number of laser systems sold in this sector.

The number of presentations of the entire Lacona series of conferences give the first indicator. The sequence is reported in the following Table 1.

Table 1: Number of papers presented as oral communications or posters to Lacona conferences

LACONA I Heraklion 1995	LACONA II Liverpool 1997	LACONA III Florence 1999	LACONA IV Paris 2001	LACONA V Hosnabrueck 2003	LACONA VI Vienna 2005
33	38	52	58	65	128

As is observed the scientific production is more that doubled during the last five years, while it was remaining steady before [3]. This production is related to a larger number of different topics, such as laser ckeaning of stone, of metals, of glass, of paintings, of organic materials, double pulse holography, laser Doppler vibrometry, LIBS, Raman spectroscopy, LIDAR, OCT, welding etc. Also the spread in European countries increased[4], involving not only Italy, Greece, UK, Germany, France, Spain, Austria, Unites States and Poland, but also newcomer activities in Netherlands, Romania, Portugal, Slovenia, Denmark, Sweden, etc.

The list of laser producers and their overall sales grew in the last five years, giving consistent results with the previous indicator. The increase of sales brought the overall number of laser systems for cleaning in Europe to more than two hundreds units. This significant number means that also conservation institutions and private restorers are buying the laser for cleaning purposes. Other laser systems employed for diagnostics remain in the research laboratories by

now, with the exception of 3D laser scannning systems for digital documentation, which is also a booming sector of activity.

Consequently the growth observed in the field of lasers in conservation can be attributed largely to the impact of the COST Action G7 on the positive evaluation given by the conservation community in Europe. Laser techniques in conservation are still a very interesting scientific issue, with significant successful applications and many open challenges offering promising fields of research. But today they are also a well accepted and appreciated professional tool in the hands of restorers. The transfer of scientific and technological findings to laser producers and also the transfer of methodology to companies offering restoration services have been a crucial objective of national and European programs. In many countries the local public institutions of conservation have been involved and now we may say that the innovation determined by lasers in conservation is definitely sustainable. This definition applies when a forced change remains in action also turning off the originating force. The innovation caused by lasers in the conservation sector is sustainable because the advantages in respect with other techniques are now demonstrated, and the improvement in the precision and control of the cleaning is actually crucial especially when a masterpiece is involved. The use of the laser tools has to be restricted to well trained restorers, causing an intrinsic demand of training courses. The cost and reliability of the laser products are now acceptable by the end-users, because the last generation of devices has improved their engineering and added a worthwhile value to their performance.

Acknowledgement

The author wishes to thank the participants to COST Action G7 “Artworks Conservation by Laser” for the availability of their results, and the COST Office for the support.

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[3] See for example Lasers in Conservation of Artworks, K. Dickmann, C. Fotakis, J.F. Asmus (Eds) Springer Proceedings in Physics n.100, Berlin Heidelberg 2005.

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European project details

COST Action G7, Arworks Conservation by Laser, Renzo Salimbeni, IFAC-CNR, Italy

TESTS OF LASER CLEANING AND DIAGNOSTICS OF MODERN PAINTINGS

Iwona Szmelter[1], Andrzej Koss[1], Jan Marczak[2], Roman Ostrowski[2], Antoni Rycyk[2], Wojciech Skrzeczanowski[2], Antoni Sarzyński[2] and Marek Strzelec[2]

[1]Inter-Academy Institute for Conservation and Restoration of Works of Art, Academy of Fine Arts, Poland
[2]Institute of Optoelectronics, Military University of Technology, Poland

The cleaning and conservation of modern art, including painted surfaces, is among the most critical operations in conservation. Several problems of their own, as difficult to control depth expansion of solvents, toxicity of the majority of the efficient liquids, insolubility of many materials as well as requiring great dexterity and lengthy mechanical interventions, need the search of alternative techniques, based on the newest scientific achievements. Laser cleaning has been evaluated as one of the most promising techniques. The advantages of laser cleaning lie in the lower risk of damage of top layers as a result of greater control of the amount and type of material removed. Moreover, lasers offer advanced diagnostic methods of works of art..

Laser cleaning systems

ReNOVA		λ [μm]	Energy max. [mJ]	Pulse duration [ns]	Repetition rate [Hz]	Laserbeam diameter [mm]
Laser 1		1,064	120	8	**1-20**	**6**
Laser 2		1,064	600	8	**1-10**	**8**
	II harm.	0,532	280			
Laser 5		1,064	1000	8	**1-10**	**10**
	II harm.	0,532	520	8	**1-10**	
	III harm.	0,355	360	8	**1-10**	
	IV harm.	0,266	180	8	**1-10**	
	V harm.	0,213	30	8	**1-10**	
LasErb 2936		2,936	2000	200 000	**1-2**	**4**

Diagnostic systems

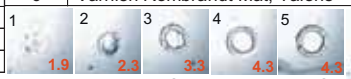
LIBS Mechelle 5000 spectrometer with iStar Dv434 camera and Quantel Nd:YAG, Q-switched laser source

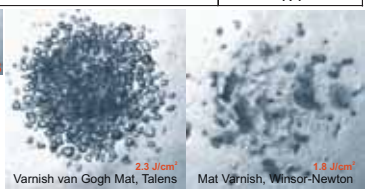
Ocean Optics Raman system R-3000

Minolta CM-2600d spectrophotometer

Determination of substrate ablation threshold (Er:YAG laser 2.94 μm; pulsewidth of 78 μs)

Quartz substrate (1.5 mm)			Polyester substrate (45 μm)		
No	Sample description	Threshold fluence [J/cm^2]	No	Sample description	Threshold fluence [J/cm^2]
1	Polyester resin dissolved in styrene + mat agent (SiO_2)	1.1	1	Varnish PMB P550-40TB, Lascaux	1.3
2	Polyester resin dissolved in styrene	2.3	2	Varnish van Gogh Mat, Talens	1.2
3	Movilith 50, Hoechst	1.4	3	Varnish Mat, Winsor-Newton	1.1
4	PMB Plextol B500, Roehm	1.3	4	Colorless Retouching Varnish, Winsor-Newton	1.9
5	Varnish PMB P550-40TB, Lascaux	2.2	5	Prefix Colorless Fixative Spray, Rowney	1.8
6	Vinyl resin, Dragon, Poland	1.0	6	Varnish Rembrandt Mat, Talens	1.4
7	Polyurethane resin, Dragon, Poland	1.5			
8	Varnish van Gogh Mat, Talens	1.1			
9	Epoxy resin	1.8			





Microscope photographs 1-5 show the procedure of determination of ablation threshold for Rowney Prefix Colorless Fixative Spray (red numbers - fluency). Photos 4 and 5 were made at different samples, showing the high repeatability of measurements for similar laser fluence. Larger photographs at the right side show the high destructivity of laser beam above the threshold in the case of mat varnishes. In general, mat substances are more sensitive (lower threshold), as it can be seen in the most cases presented in both tables.

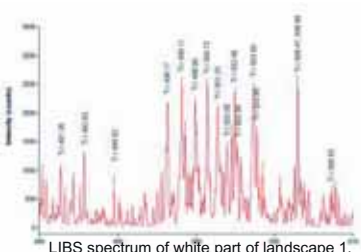
Laser ionization breakdown spectroscopy (LIBS) and Raman spectroscopy

Three numbered landscapes from the large collection of paintings of Stanisław Żukowski

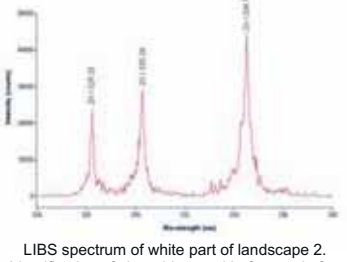
Detection head of LIBS system

LIBS adjustment

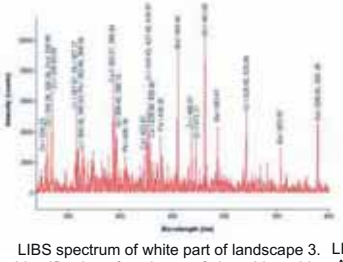
Raman head adjustment



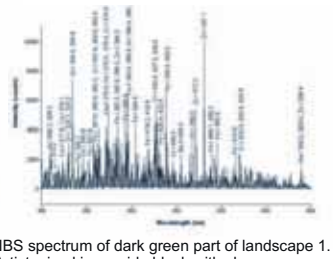
LIBS spectrum of white part of landscape 1. Identification of titanium white allowed dating of painting to be created after 1920.



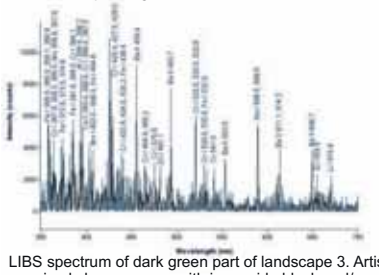
LIBS spectrum of white part of landscape 2. Identification of zinc white used before and after 1920 doesn't allow exact dating.



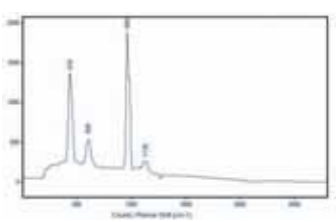
LIBS spectrum of white part of landscape 3. Identification of a mixture of zinc white, white lead and fixed white made dating imposible.



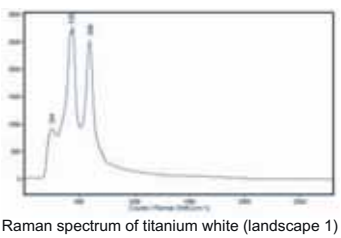
LIBS spectrum of dark green part of landscape 1. Artist mixed iron oxide black with chrome green. Substrate was mixture of zinc white and chalk.



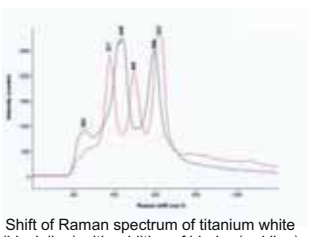
LIBS spectrum of dark green part of landscape 3. Artist mixed chrome green with iron oxide black and/or manganese black .Substrate - fixed white and chalk.



Raman spectrum of fixed white (landscape 3)



Raman spectrum of titanium white (landscape 1)



Shift of Raman spectrum of titanium white (black line) with additive of binder (red line)

All Raman spectra have been extracted from a very strong fluorescence signal emitted by binder and/or varnish.

Work has been supported by the Ministry of Education and Science, project 125/E-323/SPB/COST/H-1/DWM 85/2004-2005 and, from September 2005 EUREKA E!3843 EULASNET LASCAN project 120/E-410/SPB/EUREKA/KG/DWM 97/2005-2007

Tests of laser cleaning and diagnostics of modern paintings

Iwona Szmelter[1], Andrzej Koss[1], Jan Marczak[2], Roman Ostrowski[2], Antoni Rycyk[2], Wojciech Skrzeczanowski[2], Antoni Sarzyński[2] and Marek Strzelec[2]

[1] InterAcademy Institute for Conservation and Restoration of Works of Art, Academy of Fine Art, Poland
[2] Institute of Optoelectronics, Military University of Technology, Poland

Key words: laser cleaning, modern art, LIBS spectroscopy

Introduction and content

The cleaning and conservation of modern art, including painted surfaces, is among the most critical operations in conservation. Several problems of their own, as difficult to control depth expansion of solvents, toxicity of the majority of the efficient solvents, insolubility of many materials as well as requiring great dexterity and lengthy mechanical interventions, need the search of alternative techniques, based on the newest scientific achievements. Laser cleaning has been evaluated as one of the most promising techniques, what was proved by the earlier projects of the team connected with renovation of artworks made of various materials [1-4]. The advantages of laser cleaning lie in the lower risk of damage of top layers as a result of greater control of the amount and type of material removed. Moreover, laser offers environmentally friendly technique.

The paper presents results on laser cleaning and application of advanced diagnostic methods of modern works of art. It was described also the methodology of determination of safe range of laser energy density used for investigations of modern artistic materials and results of identification and dating tests of paints and pictures.

European dimension

The paper is focused on presentation of preliminary results of the project "Laser renovation of modern works of art" realized and financed in Poland in the frames of the COST Program, G7 Action "Artwork Conservation by Laser". The proposed works have been approved by the MC Action representatives as a trial to gather new experience in application of laser technology and photonics for protection of European culture heritage. In the project, the experienced team of conservators from the Academy of Fine Arts in Cracow and laser technology specialists from the Military University of Technology in Warsaw were employed.

Innovation and originality

The lasers have been successfully used for restoration of historical artworks for years but their application for renovation of modern artworks is at the initial stage now. Such modern artworks are frequently made by means of unconventional techniques and advanced materials. The up-to-date but not numerous information on laser technology used both for cleaning and diagnostic of objects can be found among the abstracts of recent scientific conferences [5, 6].

Laser renovation requires precise determination of a safe range of laser energy densities, i.e., above a threshold of dirt ablation and below a threshold of destruction of valuable superficial layers. During the project accomplishment, the thresholds of damages of many plastics on quartz and foil substrates were determined when they are irradiated with Er:YAG laser (2.94 μm). Figure 1 shows microscopic picture of a layer of PMM acrylic resin (van Gogh mat, serie 3, prod. Talens) after one laser shot near the threshold value.

Er:YAG laser generates infrared radiation, strongly absorbed by OH bonds with adequate small depth of penetration [7]. OH bonds can be included in residue materials on a surface or when there are only a few of them or even do not exist, they can be added in auxiliary liquids (water, alcohol). It should be pointed out that radiation of mid-infrared is much more safer for human eye than Nd:YAG laser radiation commonly used for cleaning. In cleaning processes, significantly useful would be the lasers generating the pulses shorter than 78 μs what would limit thermal interaction with objects. The works on narrowing of Er:YAG laser pulses were undertaken within the frame of the project and the constructed model of a laser head was used for initial investigations of ablation.

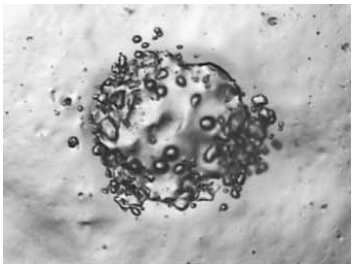


Figure 1: A sample of PMM acrylic resin on quartz substrate irradiated with Er:YAG laser fluence of 2.9 J/cm^2 and pulse duration 78 μs

Among different diagnostic techniques, LIBS and Raman spectroscopy have been used for investigations on materials identification and objects dating. Mechelle 5000 spectrometer with iStar DV434 camera from Andor Technology and Quantel/BigSky Nd:YAG, Q-switched laser have been successfully applied in LIBS experiments. In the Raman experiment, Ocean Optics system R-3000 assures spectral resolution of 6-8 cm^{-1}, when the object has been illuminated with 250 mW of 785 nm laser light. Figure 2 shows the shift of Raman spectrum of titanium white caused by the presence of binder in the paint. As the laser beam penetrates painting layers, primary ground and substrate, spectrum includes peaks characteristic for all these layers.

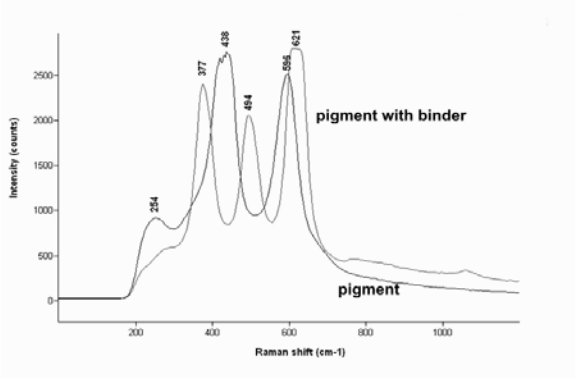


Figure 2: A Raman spectrum shift after additive of binder to titanium white pigment

Impacts

A picture in Fig. 3 shows the known method of "squares" which are irradiated with various densities of laser energy. An experienced conservator can estimate safe values of fluence on the basis of visual observation and microscopic pictures. For the case illustrated in Fig. 3, the Er:YAG laser was used for removal of a layer of old varnish under various experimental conditions.

The indentification measurements of modern artworks by means of spectroscopic methods carried out within the frame of the project can be also used for dating in spite of the fact that

such dating is not always univocal one. Among others, several Stanislaw Zukowski landscapes (from a set of not named artworks) were investigated with LIBS system. The obtained LIBS result with a short comment is shown in Fig. 4. The performed, during the project, basic investigations constitute the basis for further application works.

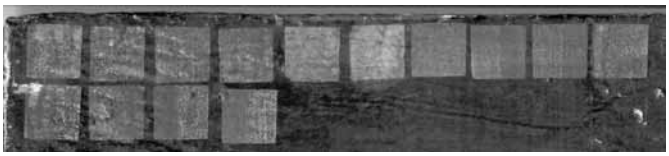


Figure 3: Old varnish removed from a painting using Er:YAG laser radiation (for various radiation energies and laser pulse durations)

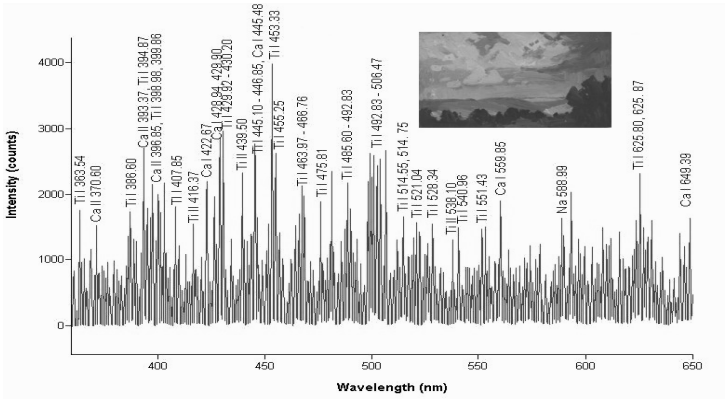


Figure 3: LIBS spectrum of white part of Stanislaw Zukowski landscape. A presence of titanium white dates the picture at the period after the year 1920. A small photograph above the peaks shows the investigated painting in a grey scale.

Acknowledgement

Work has been supported by the Ministry of Education and Science and in the frames of COST Program, G7 Action, project 125/E-323/SPB/COST/H-1/DWM 85/2004-2005.

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Laser Multitask Non Destructive Technology in Art Conservation Structural Diagnosis

IESL/FORTH

V. Tornari1, i.Bernikola1, C. Falldorf2, E. Esposito3, R. Dabu4, A. Anastassopoulos5, D. Schipper6, M. Stefanaggi7, H. Bonnici8 , D. Ursu9

1 IESL/FORTH, 2 BIAS, 3 UNIVPM, 4 NILPRP, 5 Envirocoustics S.A., 6 Art Innovation b.v, 7 LRMH, 8 MMRI, 9 ProOptica

EC 5th FWP - DG Research, EESD, LASERACT EVK4-CT-2002-00096

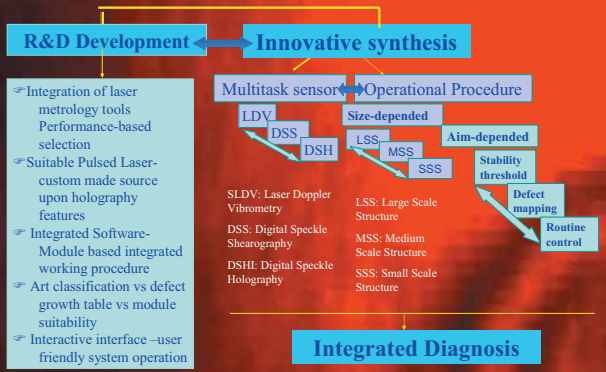
Laser metrology techniques successfully applied in industrial diagnostic fields have not yet been adjusted in accordance to the investigations requirements of Cultural Heritage applications. The setback is due to the partial applicability provided by each technique unsuited for the variety of diagnostic problems implicated in the field. The fragmented implementation have obstructed the technology transfer and elevates the aim to integrate complementary properties providing the essential functionality. In particular, structural diagnosis in art conservation intends to depict the mechanical state of the concerned cultural treasure for plotting its restoration strategy. Conventional conservation practices mostly rely on point by point finger-knocking on the exposed surfaces to differentiate acoustically from the surface sound loosely adherent layers and disbonds between surfaces. Ultimate tool for movable items and in emergency cases is considered the x-ray imaging and thermography use which mostly reveal extended material loss and inhomogeneous conservation replacement.

Modern optical metrology may provide non contacting examination with higher resolution for accurate defect localisation and comparative investigation alternatives embracing a variety of diagnostic requests which may range from defect-topography and stability threshold to routine control and environmental impact assessment.

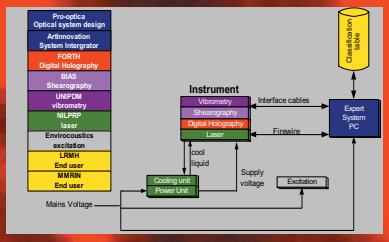
A wide range of applications for artwork conservation problems in one transportable, user-friendly, safe, sensitive and fast multi-system with a diagnostic methodology developed to integrate investigation procedures of complementary techniques. This objective is in the focus of the LASERACT project and is realised through innovative strategic synthesis of methodology- instrumentation and hardware-software development.

PROJECT OVERVIEW

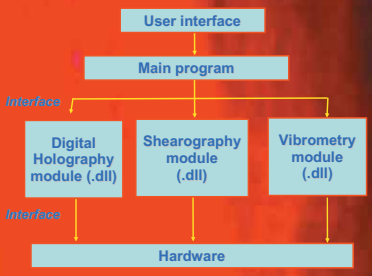
Methodology



Basic build-up hardware



Software integration



MULTITASK SYSTEM FIELD PERFORMANCE

Transportable multitask sensor for in situ measurements.

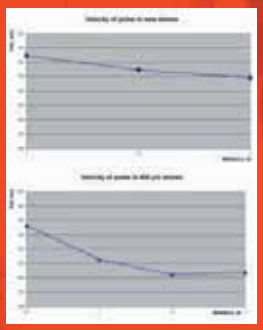
Dome-scaffolding at Victoria church, Valetta-Malta

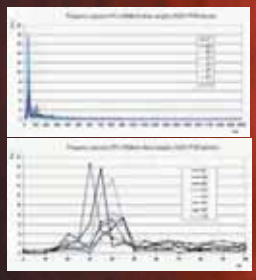
Fortification, Floriana-Malta

Defect detection

Sandstone sculpture, delamination (DSS)

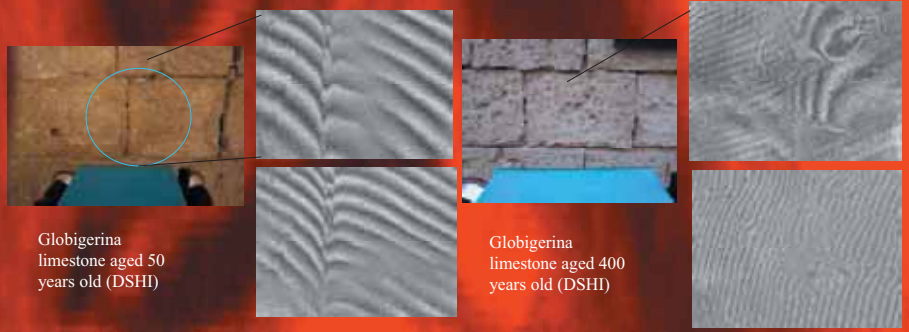
Comparative age assessment (LDV)





Frequency response of Maltese stone samples (LDV)

Comparative inspection for aged stone differentiation



Globigerina limestone aged 50 years old (DSHI)

Globigerina limestone aged 400 years old (DSHI)

PROJECT PARTNERSHIP

1. Foundation for Research and Technology/Institute of Electronic Structure and Laser, FORTH/IESL (GR), Voutes71110 Heraklion – Crete, Greece
2 Bremen Institute of Applied Beam Technology/Optical Metrology, BIAS (D) Klagenfurter Strasse, 228359 Bremen, Germany
3 Universita Politechnica Delle Marche/Department of Mechanical Engineering UNIVPM (I), Via Brecce Bianche, 60131 Ancona Italy
4 National Institute for Laser Plasma and Radiation Physics/Solid-State Laser Laboratory, NILPRP (RO), Atomistilor 111, 76900 Bucharest-Magurele Romania
5 Envirocoustics, S.AEnvirocoustics (GR), EL. Venizelou 7 & Delfon ,4452 Athens, Greece
6 Art Innovation b.v (NL), Westermaatsweg 117556 BW Hengelo, Netherlands
7 Laboratoire de Recherche des Monuments Historique, LRMH (FR), 29 rue de Paris, F-77420 Champs sur Marne, France
8 Ministry of Resources and Infrastructure/Works Division-Restoration Unit, EM/WD (MT), CMR02 Floriana, Malta
9 Societatea Comerciala PRO OPTICA S.A/ Research and Development Department, ProOptica (RO), Aleea Gh. Petrascu 474404 Bucharest Romania

Laser multitask non destructive technology in conservation diagnostic procedures

Vivi Tornari[1], Irini Bernikola[1], Claas Falldorf [2], Enrico Esposito[3], Razvan Dabu[4], Kostas Bolas[5], Dennis Schipper[6], Marcel Stefanaggi [7], Herman Bonnici[8] and Dan Ursu[9]

[1] FORTH/IESL (GR), [2] BIAS (DL), [3] UNIVPM (IT), [4] NILPRP (RO), [5] Envirocoustics S.A.(GR), [6]Art Innovation b.v (NL), [7] LRMH (FR), [8] Malta Ministry of Environment (ML), [9] Pro Optica (RO)

Key words: laser metrology, holography, shearography, vibrometry, laser, nondestructive, artwork

Introduction and content

In this project various laser interferometric techniques for structural analysis successfully applied in medical and industrial diagnostic sectors but not yet fully developed and adjusted for the field of conservation of Cultural Heritage are being considered. The drawback of fragmented applicability, in which each technique by implying distinct operational characteristics to solve specific problems disables correspondence to the complexity of diagnostic requirements involved in the field, is being faced. A strategic synthesis of operation is envisaged employing a uniquely developed investigation methodology driven by integrated software according to a custom developed hardware device. The operational specifications have been defined (1-3) to diagnose on-field a variety of artwork and monument structural problems. Invisible detachments, cracks and weakened areas steadily deteriorating the subsurface structure can be non-destructively visualised in wall and wood support paintings and Museum objects independently of surface roughness and shape complexity. Both software and hardware development requirements were elaborated by reference to an “artwork-vs-defect-classification” database formulated by the endusers of the consortium. As such the fragmented applicability of techniques involved obstructing technology know-how transfer to a new demanding field of application is confronted and a novel multitask user-friendly instrumentation is constructed particularly for extensive use in conservation of artworks (4-6). Therefore the project objective was aimed to integrate complementary advantages of techniques based on the same fundamental physical principles in one system-device capable to provide the desirable flexibility of function and standardised operation providing a user-friendly on-field transportable system as a universal structural diagnostic tool for Cultural Heritage applications.

European dimension

The project addresses a long-standing known European problem, which is certainly of major interest for the EU and beyond the frontiers of a single state. The costly and time-consuming procedure of restoration involving risks of subjective diagnosis for intervention practices and poor or wrong maintenance remains of major ethical and practical concern to European restoration authorities and city councils. Increasing deterioration of the constituents materials – be it stone, brick, wood paintings etc. – is causing great concern throughout the member states of the EU. Actions have been taken so far by European and local authorities to enhance research on conservation aspects of various art materials (stone, marble, leather, paper, etc.). Mostly relevant to historic building projects were developed to understand the causes and the mechanisms of environmental influence and to determine the conditions for prevention. Also partly to develop numerical models of examination for structural analysis with techniques such as x-ray tomography, ultrasound techniques, etc; but rather few projects the last decade assign the problem to develop equipments and systems to provide on-field assessment of the structural

condition independent of the type of Cultural heritage treasure but focused instead on the range of applications as in LASERACT project. It is the aim of the Community to provide such standards that will increase the protection and prospectively will accelerate the rehabilitation of cultural heritage in general and of artworks, historic buildings and monuments in particular. It is an aim of European dimension to maintain, safeguard and promote the pioneering role of Europe in the development and know-how transfer of advance technology to the field of Cultural Heritage research and applications.

Innovation and originality

Structural diagnostics in art conservation lacks novel technology alternative tools despite the overall technological progress in Europe that expands to all other fields of activities and applications. In this project one important reason obstructing the technology know-how transfer is confronted by the complementary use of synergetic techniques. It is assumed that this essential advance will allow and promote the wide use of laser diagnostic techniques in art conservation discipline enhancing both fields. The laser based multitask measurement technique and the developed diagnostic methodology is a total innovation in relation to the actual state of the art and to the practice of the restorer. In fact, considering first the usual manual and visual inspection and the reverberation methods a lot of time and full accessibility to the artwork is required. Also they allow only limited number of artwork to be properly diagnosed and effectively restored. Moreover, the proposed prototype providing remote sensing could be used for routine examination of endangered areas needless of complex and costly installation that prevent from periodic monitoring. Furthermore, the present manual methodology is not repeatable and does not output a record of the inspection to consist a real monitoring of the evolution in time of certain damages to assists maintenance. Another issue, which deserves attention, is the need of high sensitivity measurement techniques, to allow early detection of damage onset and permit early interventions that can reduce costs and prevent from serious deterioration. At, present the relevant high technology methodologies have no practical application; as the measurement instrument which has been applied to a number of wall-paintings, the infra-red thermography that due to its poor sensitivity and resolution and the need of producing steady temperature gradients across the structure has not met the favour of the community of restorers. Or on the other hand x-ray radiography and x-ray crystallography, apart from their special care they need due to hazardous x-ray exposure of operators, are techniques that either require surface preparation, or special ambient conditions, or removal of sample for laboratory analysis, or are partly applied to analyse the chemical composition of salts, rather than to assess directly with no additional presuppositions the structural condition of the work of art to be restored. In this context a multitask laser diagnostic measurement system implying safety and applicability for restorers and showing advantages in terms of non-intrusivity and safety, offering modulated high sensitivity and spatial resolution to adjust to the needs of the site, and the possibility offered by the current advances in laser and optics technology to construct lightweight and miniature laser and components for user-friendly transportation on-field or on scaffolding, appears as a very suited and needful tool. This has not been possible till now. A complete system which takes into account several laser based methods that are already tested and established in former collaborations pf the partners involved and that are further developed and complemented in this project to resolve the existing problem in art conservation of complex multilayered and far to reach cultural heritage treasures. The project is conceived as a progress on technology transfer of laser measurement techniques and advanced NDT to the sector of conservation diagnostics of Cultural Heritage.

Impacts

The developed prototype is under a patent-to-be process and further exploitation of the project results is scheduled by generation of a consortium spin-off with aim to optimize the pre-industrial prototype to a fully standardized industrial system for universal application. The successful outcome generates a flexible technique that would improve known optical and laser-

based diagnostic methods and strategies. The instrumentation and the technique may find immediately application in other sectors that are in need for integrated optical instruments for material testing and diagnosis. The quantitative appreciation of the economic prospect is difficult due to the particularity of developed apparatus since generates a number of potential products as device, laser, software, methodologies, and in total a novel system with long-term impact in various sectors. However in respect to the investments in the field it is safe to estimate that the devices and the laser to be produced (suitable for many industrial applications) as well as the final system for conservation diagnostics, correspond to a market size of more than 10 MEURO. Hence the LASERACT project would significantly boost the future sales of the relevant components (eg optic multitask-sensor for detection and image acquisition, software for data retrieval)-in addition to the new final product that would open a new market in a solving problem manner. A last but not least important economic impact is the variety of tools currently used in the conservation diagnostics. Conservation centres invest in diagnostic tools thousands of Euros and still their applicability is limited and fragmented. An integrated diagnostic tool flexible to adjust to the investigation demand or dimensions, shape, complexity, composition of the art object or its position can be a great benefit for cultural heritage both in ethical and economical terms.

Acknowledgement

From this point authors and partners of the consortium wish to acknowledge the realisation of the project to the European funding provided for the project LASERACT.

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European project details

LASERACT EVK4-CT-2002-00096, Laser Multitask Non-Destructive Technology in Conservation diagnostic procedures, Coordinator: Vivi Tornari, Affiliation: Institute of Electronic Structure and Laser / Foundation for Research and Technology-Hellas (IESL/FORTH), Voutes, 71 110, Heraklion, Crete, Greece, vivitor@iesl.forth.gr .

SP CHEMISTRY AND MATERIALS TECHNOLOGY: LABORATORY RESOURCE FOR CULTURAL HERITAGE PROTECTION STUDIES

Sarka Langer

SP Swedish National Testing and Research Institute
Department of Chemistry and Materials Technology
P.O.Box 857, SE-501 15 Borås, Sweden

Department of Chemistry and Materials Technology at SP comprises of experienced personnel, powerful instrumentation and exposure facilities for studies of the effects of ambient and indoor atmospheres on cultural heritage subjects. Here we list some examples some of them are illustrated in the following Figures.

- Generation of standard atmospheres of organic compounds
- GC-MS for measurements of organic compounds in air (adsorbent tubes)
- Generation and monitoring of ozone
- Exposure chambers
- APCI-MS for on-line measurements of selected atmospheric pollutants
- ToF-SIMS for surface investigations

Figure 1. Dynamic system for generation of standard atmospheres of organic compounds; with a chamber for calibration of passive samplers.

Figure 2. FLEC = Field and Laboratory Emission Cell. A microchamber for investigation of emissions of chemical compounds from surfaces and objects; also suitable for exposure, deposition and adsorption/desorption studies. The chamber is operated using an accredited method at T = 23 °C and RH = 50%.

Figure 3. The 1 m³ chamber is basically operated at room temperature of 23 °C and atmospheric pressure; in case of need it can be thermostatted between 15 – 30 °C. Relative humidity can be varied between 20 – 80 %. Distilled water is used for humidification. The temperature and relative humidity are controlled by sensors. Air change rate (ACR) can be regulated between 0.1 – 4 h^{-1}.

Figure 4. Atmospheric Pressure Chemical Ionization Mass Spectrometer with direct gas inlet for measurement of formic and acetic acids in the gas phase.

The chemical ionization occurs in corona discharge. In the negative ionization mode, negatively charged ions are formed in the primary ionization step. For example, chloride anion from chloroform, is formed in the following steps:

$O_2 + e^- \rightarrow O_2^-$

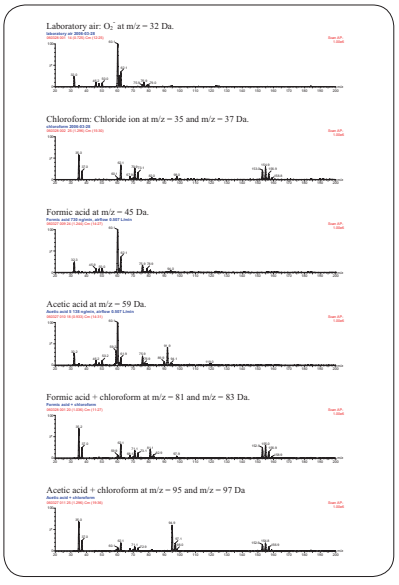
$O_2^- + CH_3Cl \rightarrow Cl^- + prod$

Formic and acetic acids form a (M-H) – parent ion: m/z = 45 and m/z = 59, respectively.

Chloride ion forms adducts with the studied molecules, in this case, with the formic or acetic acids.

$H\text{-}COOH + Cl^- \rightarrow Cl\text{-}H\text{-}COOH^-$

The adduct formation enhances the sensitivity in the measurements. In a mass spectrum of mixtures of formic or acetic acids and chloroform, several peaks are observed not only from the sub-stances present themselves, but also for the isotope relationship between ^{35}Cl and ^{37}Cl. Because of this isotope relationship, chloride-containing substances can be easily recognized and detected.



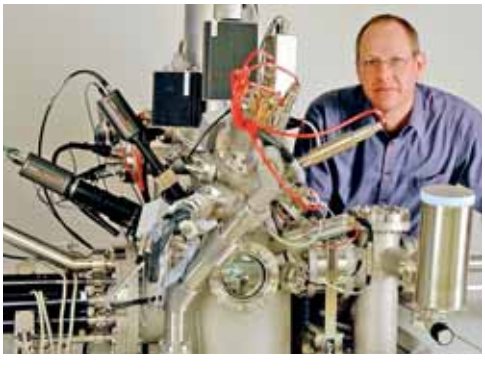


Figure 5. Time-of-Flight – Secondary Ion Mass Spectrometer is used for sensitive surface studies and imaging at nominal resolution of 2 µm.

SP Swedish National Testing and Research Institute

SP Chemistry and Materials Technology: laboratory resource for cultural heritage protection studies

Sarka Langer

SP Swedish National Testing and Research Institute, Department of Chemistry and Materials Technology, P.O. Box 857, SE-501 15 Borås, Sweden

Key words: standard atmosphere, GC-MS, APCI-MS, ToF-SIMS, exposure, emission

Introduction and content

Department of Chemistry and Materials Technology at SP comprises of experienced personnel, powerful instrumentation and exposure chambers facilities for studies of the effects of ambient and indoor atmospheres on cultural heritage subjects. Here we list some examples; some of them are described in more detail.

- Generation of standard atmospheres of organic compounds
- GC-MS for measurements of organic compounds in air (adsorbent tubes)
- Generation and monitoring of ozone
- Exposure chambers
- APCI-MS for on-line measurements of selected atmospheric pollutants
- ToF-SIMS for surface investigations

Standard atmosphere

Dynamic system for generation of standard atmospheres of organic compounds has been designed and constructed in our laboratory. The source of the organic compounds is permeation or diffusion tubes kept at constant temperature. Emission rate of the compounds is determined by periodic weighing of the tubes; the usual values are in ng/minute. The emitted amounts are mixed in a stream of air, the low is kept constant by mass flow regulators and varies between 1- 10 L/min. In this way we can obtain dynamic standard atmosphere of the desired compound in ppbv – ppmv (per volume) range.

The has been used for preparation of gaseous mixtures of volatile organic compounds for calibration using adsorbent tubes with thermal desorption and GC-MS-FID, for calibration of passive samplers and for exposure studies.

FLEC

The FLEC (Field and Laboratory Emission C, ell) chamber has been developed in a joint project between SP Swedish National Testing and Research Institute, Danish National Institute of Occupational Health and Danish Building Research Institute. It is today commercially available from CHEMATEC; for details see http://www.flec.com/.

FLEC is currently used for measurements of emissions of various compounds from flat surfaces such as flooring materials as well as from small objects. The internal volume is 0.000035 m^3 (35 ml) and the sample area is 0.0177 m^2. Smaller subjects may be introduced in a special canister with larger volume. The cell is operated according to various standards at a flow of 100 or 300 ml/minute, at a temperature of 23 ± 2 ^oC and relative humidity of 50 ± 5 % and atmospheric pressure. Cleaned and dried air is circulated above the surface and the emitted compounds are sampled. FLEC complies with ISO 160010.

Various sampling devices may be connected to the chamber, e.g. adsorbent tubes for volatile organic compounds or cartridges for sampling of aldehydes or organic acids. Results are emission factors in units of μg/(m^2*hour). Potential new use of the FLEC is studies of processes on surfaces such as chemical reactions, exposure and adsorption / desorption processes. A reacting gas or exposing gas is introduced in the circulating air and the emitting compounds are sampled and analyzed by suitable techniques.

1 m^3 chamber

The chamber is originally developed and designed for measurements of emission of volatile organic compounds (VOC) and formaldehyde from materials. The chamber is made of electropolished stainless steel with inner dimensions 65 × 102 × 150 cm (breadth × length × height). The volume of the chamber is 0.9945 m^3. It was also checked by measurement with a tracer gas (N_2O) with a result of 0.99 m^3. The internal surface is 6.337 m^2 thus giving the surface to volume ratio S/V = 6.37 m^{-1}. The chamber is equipped with several inlets / outlets for introduction of gaseous reactants and for connection of sampling devices. A circulation (squirrel cage) fan for internal mixing is placed in the bottom part of the chamber.

The chamber can be operated either in static or a dynamic mode. Dried and filtered air is supplied through a separate line; the flow is controlled by a flowmeter and measured by a volume meter. Air change rate (ACR) can be regulated between 0.1-4 h^{-1}. The chamber can be basically operated at room temperature of 23 ºC and atmospheric pressure; in case of need it can be thermostatted between 15-30 ºC. Relative humidity can be varied between 20-80 %. Distilled water is used for humidification. The temperature and relative humidity are controlled by sensors. Air and gaseous components are supplied to the chamber through a mass-flow controlled system (model 5850S, Brooks Instruments) and Teflon® lines.

The chamber can be used for emission measurements of organic compounds from materials, as well as a reaction chamber or an exposure chamber.

Atmospheric pressure chemical ionization mass spectrometry

In order to overcome the problems with both the sampling time and detection limits, Atmospheric Pressure Chemical Ionization – Mass Spectrometry APCI-MS (and also APCI-MS-MS) can be used to measure concentrations of trace gases in real time measurements. This technique unifies the advantages of sampling at atmospheric pressure with on-line measurement (time resolution of ~ 1second) and with the mass spectroscopic characterization of the measured species. The APC ionization utilizes corona discharge to primarily ionize other chemical species, which in turn, ionize the compounds of interest. The ionization may be carried out either in positive or negative ionization mode.

The chemical ionization occurs in corona discharge. In the negative ionization mode, negatively charged ions are formed in the primary ionization step. For example, formic and acetic acids form a $(M-H)^-$ parent ion: m/z = 45 and m/z = 59, respectively. Chloride anion from chloroform, is formed in the following steps:

$$O_2 + e^- \rightarrow O_2^-$$
$$O_2^- + CH_3Cl \rightarrow Cl^- + \text{prod}$$

Chloride ion forms adducts with the studied molecules, in this case, with the formic or acetic acids.

$$H\text{-}COOH + Cl^- \rightarrow Cl\text{-}H\text{-}COOH^-$$
$$H_3C\text{-}COOH + Cl^- \rightarrow Cl\text{-}H_3C\text{-}COOH^-$$

The adduct formation enhances the sensitivity in the measurements. In a mass spectrum of mixtures of formic or acetic acids and chloroform, several peaks are observed not only from the substances present themselves, but also for the adducts m/z = $(M+35)^-$ and $(M+37)^-$; isotope relationship between ^{35}Cl and ^{37}Cl enhances the selectivity of the measurements.

Calibration procedure for on-line measurements of formic and acetic acids in the gas phase is currently under way and is intended to be used together with the FLEC chamber.

Time-of-flight – secondary ion mass spectrometry

The ToF-SIMS instrument is used for sensitive surface studies. It comprises the advantages of microscopy and mass spectrometry for surface imaging.

European dimension

This contribution presents a comprehensive laboratory resource for studying the effects of atmospheric pollutants on cultural heritage subjects. The combination of the described facilities and methods has the potential of contributing to future European research projects.

Innovation and originality

The innovative aspect and originality of the results lies in the combination of exposure facilities with unique, novel and untraditional measurement methods of gaseous air pollutants (often with corrosive potential) on materials with techniques for characterization of the affected surfaces and changes invoked by the atmospheric air pollution.

Impacts

The impact of the presented research lies in providing the cultural heritage protection community with novel and sensitive investigation techniques for understanding the mechanisms and effects of gaseous components on art subjects.

For more information, please visit: http://www.sp.se/eng/materialteknik/default.asp .

DE-MS AND GC/MS TO CHARACTERIZE TRITERPENOID RESINOUS MATERIALS FROM ARCHAEOLOGICAL FINDINGS

Maria Perla Colombini, Francesca Modugno, Erika Ribechini

Dipartimento di Chimica e Chimica Industriale, University of Pisa, Pisa, Italy

Chemical studies on resinous materials in archaeological remains are generally aimed at identifying the origin of the material and studying the production and manufacturing techniques. Natural terpenoid resins and resinous materials played a prominent role, since their intrinsic properties favoured their use not only as adhesives, hydro-repellents, coating and sealing agents, but also as flavours, incense, ingredients for cosmetics, medicines, and mummification balms.

The chemical analysis of resinous substances in archaeological artefacts is generally based on the principle of "chemotaxis", that is on the presence of specific compounds (molecular biomarkers) which have survived ageing or which have been formed over the centuries as stable products of the ageing processes. The molecular biomarkers are related to:

-the botanical source from which the resin or the pitch was obtained;

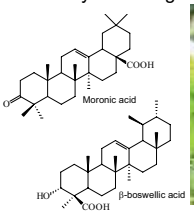
-the artificial transformations deliberately induced by man before the use of the material;

-the transformations caused by environmental factors and/or ageing, which help to shed light on the degradation processes undergone by the materials.

Two analytical techniques, direct exposure electron ionisation mass spectrometry (DE-MS) and gas chromatography/mass spectrometry (GC/MS), were used for the analyses of archaeological triterpenoid resinous substances.

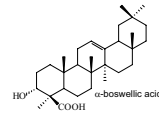
Triterpenoid materials

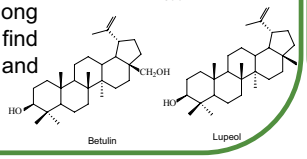
Natural resins are substances with a high viscosity, semisolids or solid and insoluble in water. They are formed in the so-called "resiniferous canals" of several trees. Many varieties of plants spontaneously exude resins as a product of their metabolism, to protect themselves against excessive loss of water and attacks by micro-organisms.



From a chemical point of view, vegetable resins are a complex mixture of mono-, sesqui-, di- and triterpenes, which have respectively 10, 15, 20, and 30 carbon atoms per molecule. The mono- and sesquiterpenes are both present in most resins.

Since di- and triterpenes are rarely found together in the same resin, resins can be divided into two main classes. Among triterpenoid resinous materials we can find **mastic resin, frankincense resin** and **birch bark pitch.**



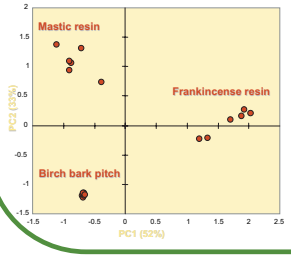


Analytical protocol for the analysis of triterpenoid resinous materials

SAMPLE

DE-MS → chemometric evaluation of mass spectral data

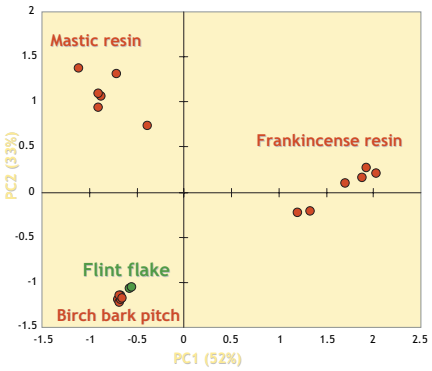
GC/MS → detection of molecular markers



Resinous material	GC/MS-Markers
Mastic resin	moronic acid, masticadienonic acid, *iso*-masticadienonic acid
Frankincense resin	α- and β-boswellic acids
Birch bark pitch	betulin, lupeol, betulone, lupenone

Adhesive material on Palaeolithic stone tools

Late Middle Pleistocene sediments of a clay pit in Italy yielded one stone tool with typological characteristics of the acheulean lithic industry. The tool was largely enclosed in blackish organic material attributed to a residue of the original hafting adhesive.

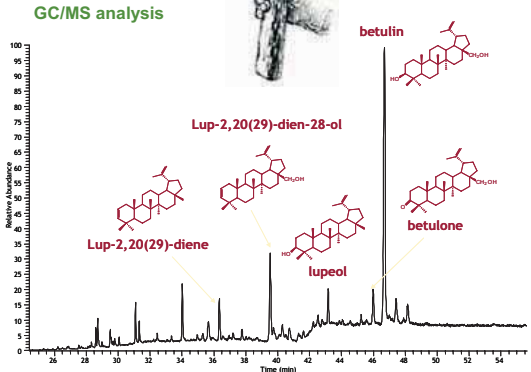


The PCA analysis performed on mass spectral data places the sample from flint flake very close to the birch bark pitch cluster.

The overall results show that the organic material recovered on the flint flake is a pitch obtained by a pyrolysis type process of birch bark.

The material was interpreted as being a residue of the original adhesive for hafting the flint flake, i.e. for assembling the lithic part of the tool with a wooden handle.

GC/MS analysis



The GC/MS analysis reveals that the sample is principally made up of triterpenoids with a lupane skeleton, betulin being the main constituent followed by lupeol, lupadienol, betulone and lupadiene.

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DE-MS and GC/MS to characterise triterpenoid resinous materials from archaeological findings

Maria Perla Colombini, Francesca Modugno and Erika Ribechini

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35-56126 Pisa, Italy

Key words: organic mass spectrometry, triterpenes, archaeological findings

Introduction and content

Knowing what features a material has, and discovering how that material can be used, has over the centuries enabled human beings to have the basic necessities of everyday life. In the past, humans tended to turn to nature as the main, and in some cases the only, source of the materials and substances that they needed: colorants, adhesives, coating, cosmetics, and medicines. Ceramic and glass objects were largely employed for processing and storing materials and substances and also used for cooking and containing food. Moreover, adhesives and coatings were often employed for finishing or repairing pottery. Consequently, traces of organic materials can occur as preserved surface residues in these containers and as adsorbed residues in porous ceramic vessels. Recent analytical investigations of amorphous organic residues have proved to be of great importance from an archaeological point of view [1-3].

Because of the complexity of these organic residues, analytical procedures used to characterize them are usually based on mass spectrometry due to its ability in obtaining detailed compositional information [4-10]. Moreover, the possibility to couple mass spectrometry with chromatographic techniques represents a further enhancement. In fact, these hyphenated techniques allow the identification at molecular level, thus revealing the presence of specific compounds acting as bio-molecular markers, which are diagnostic stable molecules present in the ancient material or formed over the centuries due to ageing.

This paper describes a chemical analytical study on vegetable tritepenoid resinous materials. The aim is to improve knowledge of these materials and their behaviour with aging, and to identify them in amorphous organic residues recovered in archaeological findings. Two analytical approaches both based on mass spectrometry were employed: direct exposure-mass spectrometry (DE-MS) and gas chromatography / mass spectrometry (GC/MS) [8-10]. DE-MS analysis gives an excellent fingerprint of the sample as well as information on the main constituents present, and GC/MS gives detailed compositional information at a molecular level and highlights a wide range of classes of natural organic compounds. The use of both these analytical techniques on two different aliquots of the same sample provides complementary information, and enables the organic materials present in the object to be reliably recognized. The main aims of the research can be summarises as follows: to assess the performance of two analytical approaches, DE-MS and GC/MS, in the study of archaeological amorphous organic residues; to select molecular markers for a reliable identification of vegetable resins in archaeological findings; to study the alteration processes that have (naturally or anthrophogenically) modified the original composition of the materials; to identify the kind of material present in the various archaeological objects and consequently, to understand the function of the organic materials and that of the objects.

European dimension

The advancement in the analytical methodologies available for the study of archaeological materials as organic residues has widespread applicability in archaeological science, and the passionate study and research on the antique civilisations is a peculiarity of European culture since centuries.

Identifying specific materials from molecular patterns can assist in assessing the role that organic substances played and in determining the use of artefacts on which these residues survive. Consequently, the chemical study of these residues can improve our knowledge of the societies of the past in Europe and in the Mediterranian area, as far as it concerns crafts and technologies, trade routes, diet, scientific advancement and religious rituals.

Innovation and originality

Through chemical analysis of the materials recovered from archaeological sites, the chemistry has become a partner with the archaeology. This partnership has existed for more than a hundred years, but only recently it included organic materials as well as inorganic ones.

Impacts

The application of the described analytical approach has permitted to contribute to the knowledge of archaeological objects from different contexts by the elucidation of the composition of organic materials.

For example, the chemical study of organic substance recovered on a Palaeolithic lithic tool showed that organic material is a pitch obtained by a pyrolysis type process of birch bark [11]. The material was interpreted as being a residue of the original adhesive for hafting the flint flake that is for assembling the lithic part of the tool with a wooden handle.

The examination of organic residues found in pottery vessels from the archaeological site of North necropolis of Antinoe highlighted a wide range of organic materials and substances. In particular, the analysis of the residue from a censer demonstrated the occurrence of mastic resin together with pine resin and a vegetable oil [11]. These results reveal the use of a mixture of substances, with a compositional complexity greater than has been previously reported in censers. Clearly, it is not possible to establish if all the identified substances were intentionally mixed or if they belong to residues of previous uses of the censer. It is not surprising that the pleasant aromatic scent of many resins under burning conditions made them suitable to be used as incense. In fact resins diffuse their aroma through smoke and smoulder slowly.

Acknowledgement

The authors would like to thank Dr. Gianna Giachi and Dr. Maria Cristina Giudotti (Archaeological Superintendence of Tuscany, Restoration Laboratory, Florence, Italy), and Dr. Giovanna Menci (Istituto Papirologico “Girolamo Vitelli”, Florence, Italy).

The financial support of the Italian Ministry for University and Scientific and Technological Research is gratefully acknowledged.

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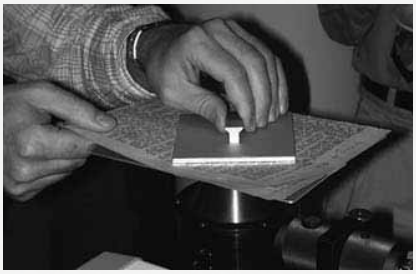
ASSESSING THE PRESERVATION STATE OF LARGE COLLECTIONS: THE *SURVE*NIR PROJECT

M. Strlič[1], J. Kolar[2], T. Trafela[1], D. A. Lichtblau[3], M. Anders[3], G. de Bruin[4], T. Steemers[4], B. Knight[5], G. Martin[6], J. Palm[7], N. Selmani[8], M. C. Christensen[9]

[1]*University of Ljubljana, Slovenia*
[2]*National and University Library of Slovenia, Slovenia*
[3]*Zentrum für Bucherhaltung GmbH, Germany*
[4]*Het Nationaal Archief, The Netherlands*
[5]*The British Library, U.K.*
[6]*Victoria and Albert Museum, U.K.*
[7]*Riksarkivet, Sweden*
[8]*State Archives of Dubrovnik, Croatia*
[9]*National Museum of Denmark, Denmark*

Millions and millions of paper-based objects worldwide are in need of conservation treatments. Which ones? How to evaluate long-term risks? How to plan large-scale preservation actions? SurveNIR aims at answering these questions.

The coat of arms of the Republic of Dubrovnik from the collection of the State Archives of Dubrovnik. This important collection will be surveyed using the new *Surve*NIR instrument.



Non-destructive assessment of paper properties could be as easy as this in the near future. The NIR spectroscopic approach will provide data on the chemical and mechanical properties, on the basis of which an informed decision making will be possible.

*Surve*NIR

Assessment of the state of archival, museum and library collections is a task of utmost importance. Depending on the type and size of a collection, surveying may also be one of the most demanding tasks in terms of the necessary resources. It is usually done using simple physical and chemical tests, often destructive, in order to reveal the collection condition, the general conservation needs and in order to plan preservation activities.

The SurveNIR project will develop a near-infrared-spectroscopic instrument, with which the end-users will be provided with an objective survey tool allowing reagent-less multi-component low-cost analysis of items.

Surveying is indispensable in the sustainable impact assessment especially of protection treatments and provides information relevant for development of preservation and research priorities of large collections.

Traditionally, the state of a collection is assessed visually, and simple physical and chemical tests are performed, such as the Stanford folding test or determination of pH of paper using pH-indicator pens. Although these traditional methods are invasive or destructive they are necessary in order to reveal the condition of a collection, the general conservation needs and in order to plan preservation activities. The SurveNIR project was started with the intention to provide museums, libraries and historic collections with a non-destructive chemical-free low-cost surveying tool that would provide even more in-depth information as the traditional methods but would also be user-friendly and would not require extensive technical knowledge of the surveyor.

It is planned that the new instrument will be used to measure paper pH, degree of polymerization (molecular weight of cellulose in paper), carbonyl group content, mechanical properties such as zero span, presence of lignin, etc. These data often serve to plan conservation actions to be undertaken. The results will be compared with the results acquired with traditional methods. Case studies in seven collections from seven European countries belonging to three widely different types of paper-based collections museum, library and archive will be performed to validate the approach.

Project webpage

http://www.science4heritage.org/survenir/

European project details

*Surve*NIR, SSPI-006594, Near Infrared Spectrosopy Tool for Collection Surveying

Coordinator: Matija Strlič, University of Ljubljana, Slovenia, e-mail: matija.strlic@fkkt.uni-lj.si

Acknowledgement

The authors gratefully acknowledge the support of the European Community, 6th Framework Programe, contract no. SSPI-006594 (SurveNIR). The work is the sole responsibility of the authors and does not represent the opinion of the Community. The Community is not responsible for any

Assessing the preservation state of large collections: SurveNIR project

Matija Strlič[1], Jana Kolar[2], Tanja Trafela[1], Dirk Andreas Lichtblau[3], Manfred Anders[3], Gerrit de Bruin[4], Ted Steemers[4], Barry Knight[5], Graham Martin[6], Jonas Palm[7], Nikša Selmani[8] and Mads Christian Christensen[9]

[1] University of Ljubljana, Ljubljana, Slovenia
[2] National and University Library, Ljubljana, Slovenia
[3] Zentrum für Bucherhaltung GmbH, Leipzig, Germany
[4] Het Nationaal Archief, The Hague, The Netherlands
[5] The British Library, London, UK
[6] Victoria & Albert Museum, London, UK
[7] Riksarkivet, Stockholm, Sweden
[8] Dubrovnik State Archives, Dubrovnik, Croatia
[9] Nationalmuseet, Copenhagen, Denmark

Key words: cultural heritage on paper, collection surveys, near infrared technology, analytical instruments

Introduction

Assessment of the state of collections is a task of utmost importance in any archive, museum or library. Depending on the type and size of a collection, surveying may also be one of the most demanding tasks in terms of the necessary resources. It is usually done using simple physical and chemical tests, which are often invasive or destructive.

The objective of the SurveNIR project is to provide an innovative, stat-of-the-art new near-infrared-spectroscopic instrument, with which the end-users will be able to rapidly and objectively determine the state of preservation of a large number of documents. As a result of the reagent-less multi-component low-cost analysis, the collection manager will be given data on the basis of which preservation actions can be planned. Such surveying is indispensable in the sustainable impact assessment of protection treatments and provides relevant information for development of preservation and research priorities of large collections.

The tool will be tested in seven European collections of major importance, thus validating the developed approach.

European dimension

Paper-based documents have long been, and still are, witness to human activity. Fortunately, paper is a long-lived material provided that the production technology favours its stability, and provided that it is stored in a favourable environment.

In the 19th century, paper was a global commodity. Not only was it used for printing and writing, but also for clothing and even coffins were made of it. No wonder that the consumption soon outgrew the supply. Straw, bark and even peat were used for papermaking, due to the lack of raw materials. The old ways of production, using high quality linen or hemp fibres and gelatine sizing, were replaced by industrial production of acid-sized paper made of wood fibres. The low quality of fibres and especially sizing with rosin, which was precipitated on fibres using papermaker's alum, an acidic substance, contributed to the fragility of the new type of paper. The lifetime was suddenly reduced from several thousand years, to merely a century or two.

Today, we are faced with vast numbers of documents from ca. 1850-1990, which are extremely endangered. For documents produced around 1900, it has been estimated that they are likely not to survive another century. Basically, the era encompassing two world wars, and major revolutions in science, art and society, may become a new dark age unless a large-scale mass preservation action is taken on the European scale.

Innovation and originality

The innovative technological aspect of the SurveNIR instrument is in that it will enable the end-user to analyse paper mechanical and chemical properties non-destructively using near infrared spectroscopy enhanced with advanced chemometrics. Basing on thousands of real measurements, the chemometric models, now in the development phase, will predict paper properties on the basis of a near infrared spectrum. The spectrum can be taken in a matter of seconds, even by an end-user without formal scientific training. The instrument itself has already been produced and is currently being tested. The lightweight portable instrument can easily be carried to be used in any collection.

The particular advantage of the SurveNIR approach is that it is easy to foresee the technology to be transferred to other areas of conservation research, e.g. parchment, textiles, leather, etc.

Impacts

While the assessment of mass preservation actions is the focus of another 6th Framework project PaperTreat (www.science4heritage.org/papertreat), collections first need to be surveyed, in order to assess the dimensions of the problem of decaying European paper-based collections. Using the new SurveNIR instrument, planning will be enabled on the basis of real data, such as what part of a collection is on acidic paper, or made of low quality lignin-containing fibres etc.

The instrument will be marketed by Zentrum für Bucherhaltung GmbH, and accessible to all European libraries, museums and archives. In order to validate the approach, the consortium will also perform several pilot surveys of important European collections.

As part of the dissemination strategy, a workshop will be organised in spring 2008, accompanied by a booklet on surveying paper-based cultural heritage using near-infrared technology.

References

[1] SurveNIR webpage, http://www.science4heritage.org/survenir/

European project details

SurveNIR
SSPI-006594
Near Infrared Spectroscopy Tool for Collection Surveying.
Coordinator: Matija Strlič, University of Ljubljana, Slovenia, e-mail: matija.strlic@fkkt.uni-lj.si

USE OF THERMAL, SPECTRAL AND SCANNING ELECTRON MICROSCOPY METHODS TO ASSESS THE DAMAGE OF ROMANIAN HERITAGE LEATHER AND PARCHMENT OBJECTS

Lucretia Miu (1), Petru Budrugeac (2), Maria Giurginca (3), Aurelia Meghea (3), Nicoleta Badea (3), Carmen Gaidau (1), Doina Seclaman (4)

(1)Leather and Footwear Research Institute, 93 Ion Minulescu str, 031215, sector 3, Bucharest, Romania
(2) INCDIE-ICPE-CA Bucharest, 313 Splaiul Unirii, 030138, sector 3, Romania
(3)Polytechnic University of Bucharest, 1 Polizu str., 011061, sector 6, Romania
(4)History National Museum of Romania Bucharest, 12 Calea Victoriei, sector 3, Romania

Introduction and Content

Thermal analysis methods (TG, DTG and DTA), scanning electron microscopy (SEM), spectral methods (IR, UV-VIS-NIR) and shrinkage temperature have been used to assess the damage level in some collagen based materials from Romanian heritage objects in comparison with new manufactured leathers and parchments. Similar methods were performed in European research projects on different kind of old leather and parchment from UE area [1-3].
When thermal analysis methods (by progressive heating in air) were used, all investigated materials revealed three main successive processes associated with dehydration and thermo- oxidative degradation. The thermal behaviour of the recently manufactured leathers and parchments was compared with that of the heritage collagen based materials. The thermal-oxidative rate has revealed to be possibly correlated with the natural damage level of leather. SEM provided information on the leather morphology, shape of leather fibre patches and structure of individual fibres. In the IR domain the bands of amide structure I and II (1652 and 1450 cm-1) are modified, while in UV-VIS-NIR domains some changes in intensity of bands 480 500 nm domain could be noticed and assigned to a higher content in oxygenated structure that causes the change in the chromatic characteristics.

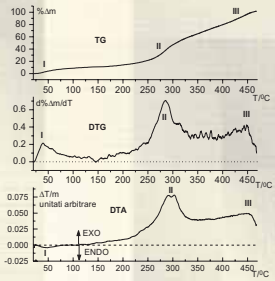


Fig. 1. The thermal analytical plots for the new goat leather

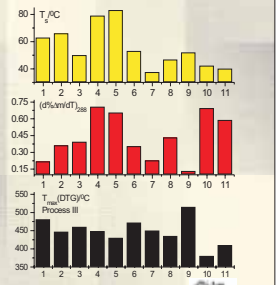


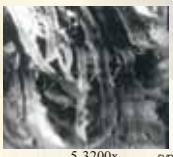
Fig. 2. Shrinkage temperatures (T_s); $\left(\frac{d^2\%.\Delta m}{dT^2}\right)_{max}$ for process II and the temperature corresponding to maximum reaction rate of process III (T_{max}(DTG)) for old and new leathers and parchments

Experimental

The samples of leathers and parchments investigated in the paper are presented in table 1.
Table 1- Old and new leather and parchment samples

Symbol	Sample	Origin
1	New parchment	ICPI, kid
2	New parchment	ICPI, calf
3	Old parchment (Ton Basilicon)	MMB**
4	New leather	ICPI, goat
5	New leather	ICPI, sheep
6	Old leather (Romanian armour from XVI century)	MMNB*
7	Old leather (belt from 1837)	MMNB*
8	Old leather (Austrian belt 1860)	MMNB*
9	Old leather (bag for gun powder XIX century)	Mina Minovich Museum***
10	Old leather (book cover XIX century)	MMB**
11	Old leather (sheath of an oriental sword)	MMNB*

*MMB-Military National Museum - Bucharest, **MMB-Municipal Museum - Bucharest***Mina Minovich Museum-Bucharest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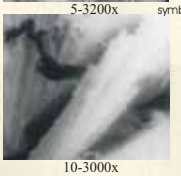
symbol - magnification


6-3200x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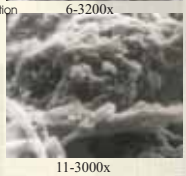
11-3000x

Thermal analysis and shrinkage temperature

The thermal degradation of new and old leathers and parchments occurs through three main successive processes accompanied by mass losses. Figure 1 shows the TG, DTG and DTA curves for the new vegetable goat leather (symbol 4). Similar plots have been obtained for all analysed samples. The first process (denoted by I) is an endothermic one and takes place in the temperature range of 25°C to 125°C. This consists of the loss of water contained by each investigated material. The second and the third processes (denoted by II and III) are exothermal ones and consist of the decomposition and thermo-oxidation of the material. Some volatile products with low molecular weight are also released during process III. In our opinion, about many series of determinations, the assessment of leathers and parchments damage is expressed through processes II and III. The characteristics of the processes II and III as well as the shrinkage temperatures (micro hot table method) are comparatively shown in Figure 2.
The inspection of these curves shows that: (a) for old leathers Ts are lower than those corresponding for new leathers and comparable with that obtained for parchments; (b) the old leathers can be classified in two groups, namely: (1) the old leathers for which $\left(\frac{d^2\%.\Delta m}{dT^2}\right)_{max}$ (proportional with the reaction rate), have values between those corresponding to parchments and new leathers, and T_{max}(DTG) higher than 435°C (samples 6 -9); (2) the old leathers for which $\left(\frac{d^2\%.\Delta m}{dT^2}\right)_{max}$ have values closed to those corresponding to new leathers, and T_{max}(DTG) lower than 405°C (samples 10 and 11). The behaviour of samples 10 and 11 suggests a deep level of degradation which is in accord with visual and SEM assessment. These behaviours could be associated with the natural degradation of the old and much damaged leathers.

Scanning Electron Microscopy

The most significant SEM analyses of the investigated samples were intended to characterize the cross section, by revealing the structural changes occurring in fibers showing the preservation condition and fibrile damage level. The SEM images of the old leathers (6,10,11) in comparison with new one (5) reveal the following: flattened papillary layer which cannot by distinguished from the reticular layer; stuck together, flattened and thinned collagen fibers; lack of the interfibrilar gaps because of the compaction.

Spectral analyses ((IR, UV-VIS-NIR)

Significant IR spectral characteristics are the most relevant of them being those originating from the valence and deformation vibration of amide structure (3418, 1656 and 1546 cm-1) and carbonyl/carboxyl groups(1735 cm-1). These spectral modifications are characteristic for assessing the collagen support damage level in natural conditions (Table 2).
Table 2-The characteristics for assessing the collagen support damage level

Symbol	$R=A_{1655}/A_{1545}$	Δν (amide I -amide II)	$R=A_{1735}/A_{1655}$
1	1.00	101	-
2	1.00	98	-
3	1.10	108	-
4	1.00	96	-
5	1.05	97	-
6	1.20	111	-
7	1.44	113	0.71
8	1.400	111	
9	1.318	109	0.48
11	1.182	95	0.50

There are great differences between the bands assigned to the amide structures (1655 and 1545 cm^{-1}) and valence/deformation ratios for the samples of old leather and parchment and those of newly made ones. All the samples of old leather and parchment show higher values for the amide I and II absorbance ratios and for Δν, in comparison with new leathers, excepting sample 11. Only three of these samples show oxygenated groups of carbonyl/carboxyl type (9, 7, 11). In the UV-VIS-NIR spectra, samples show typical bands for the π→ π* and n→ π* transitions proper to the amide groups and oxygenated structure of N=O type at 655/675 nm, as well as to harmonics and combination bands in IR medium spectra from the same structures.The recorded spectra have enabled the colour characteristics to be determined by means of the CIE-Lab software.

European dimension

Assessment of damage level of leather and parchment from Romanian patrimony objects will contribute to European enrichment of acknowledgments in the field.

Innovation and Originality

In our opinion, about many series of determinations, the assessment of leathers and parchments damage is significantly expressed through processes II and III of thermal analyses (TG, DTG and DTA). Absorption spectra techniques (FT-IR and UV-VIS) have identified the amide structure changes as the result of the natural ageing of old leathers.

Impacts

The paper offers new information which completes the visual assessment of damage level of old leathers and parchments through the identification of some specific parameters of thermal and spectral analyses.

Acknowledgement

The authors are gratefully acknowledge to Romanian CALIST Research Programme, Magda Souckova from National Library of the Czech Republic, Ghiocel and Aurelia Ioanid from Institute of Macromolecular Chemistry "Petru Poni" Iassy, Romania

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Use of thermal, spectral and scanning electron microscopy methods to assess the damage of Romanian heritage leather and parchment objects

Lucretia Miu[1], Petru Budrugeac[2], Maria Giurginca[3], Carmen Gaidau[1], Aurelia Meghea [3], Nicoleta Badea[3] and Doina Seclaman[4]

[1] Leather and Footwear Research Institute, 93 Ion Minulescu str, 031215, sector 3, Bucharest, Romania
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[4] History National Museum of Romania –12 Calea Victoriei, sector 3, Bucharest, Romania

Key words: patrimony leather and parchment damage, thermal analysis, spectral analysis, SEM, T_S test

Introduction and content

Thermal analysis methods (TG, DTG and DTA), scanning electron microscopy (SEM), spectral methods (IR, UV-VIS-NIR) and shrinkage temperature have been used to assess the damage level in some collagen based materials in Romanian heritage objects in comparison with new manufactured leathers and parchments. Similar methods were performed in European research projects on different kind of old leather and parchment from UE area [1-3].

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Experimental

The samples of leathers and parchments investigated in the paper are presented in table 1 (see poster page).

Thermal analysis and shrinkage temperature

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The inspection of these curves shows that: (a) for old leathers T_s are lower than those corresponding for new leathers and comparable with that obtained for parchments; (b) the old leathers can be classified in two groups, namely: (1) the old leathers for which $(\frac{d\%\Delta m}{dT})_{288}$ (proportional with the reaction rate), have values between those corresponding to parchments and new leathers, and T_{max}(DTG) higher than 435^{0}C (samples 6-9); (2) the old leathers for which $(\frac{d\%\Delta m}{dT})_{288}$ have values closed to those corresponding to new leathers, and T_{max}(DTG) lower than 405 ^{0}C (samples 10 and 11). The behaviour of samples 10 and 11 suggests a deep level of degradation which is in accord with visual and SEM assessment. These behaviours could be associated with the natural degradation of the old and much damaged leathers.

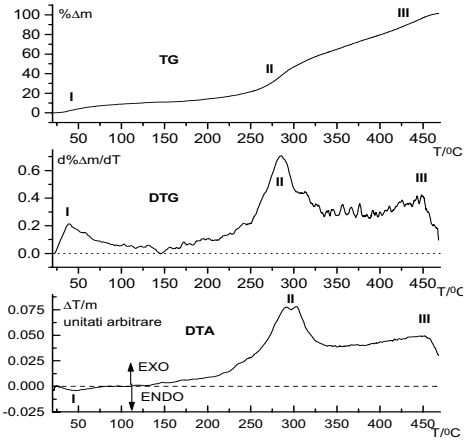


Figure 1: The thermal analytical plots for the new goat leather

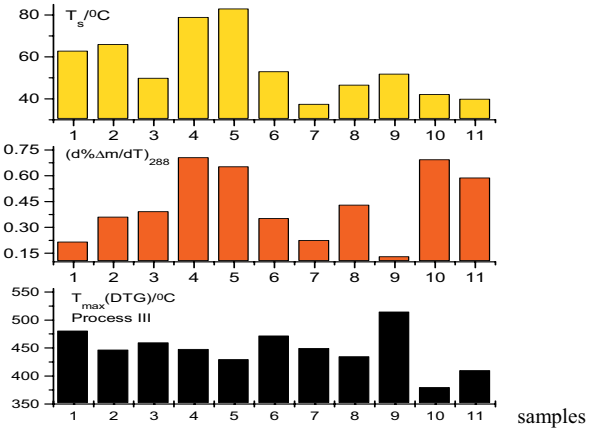
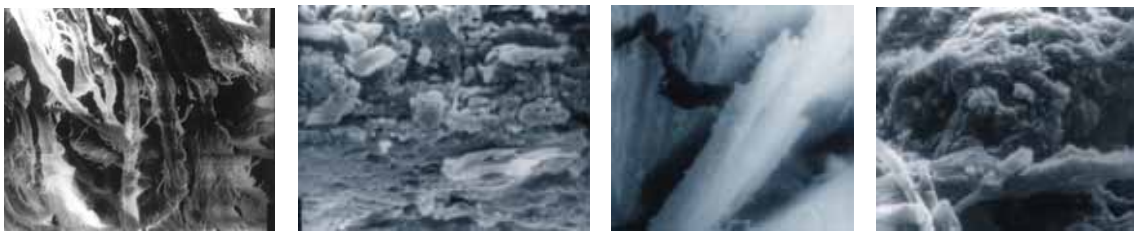


Figure 2: Shrinkage temperatures (T_s); $(\frac{d\%\Delta m}{dT})_{288}$ for process II and the temperature corresponding to maximum reaction rate of process III (T_{max}(DTG)) for old and new leathers and parchments

Scanning electron microscopy

The most significant SEM analyses of the investigated samples were intended to characterize the cross section, by revealing the structural changes occurring in fibers showing the preservation condition and fibers damage level. The SEM images of the old leathers (6,10,11) in comparison with new one (5) reveal the following: flattened papillary layer which cannot by distinguished from the reticular layer; stuck together, flattened and thinned collagen fibers; lack of the interfibrous gaps because of the compaction.



Symbol-magnification: 5-3200× *6-3200×* *10-3000×* *11-3000×*

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Impacts

The paper offers new information which completes the visual assessment of damage level of old leathers and parchments through the identification of some specific parameters of thermal and spectral analyses.

Acknowledgement

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DAMAGE ASSESSMENT OF PARCHMENT: THERMONALYTICAL (macro-nanoscale)& NON-INVASIVE SPECTROSCOPIC ANALYSIS

M. Odlyha[1], C. Theodorakopoulos[1], J.de Groot[1,2],L.Bozec, M.Horton, Q.Wang[3], G.M.Foster[4] and R.Campana[1]

1. School of Biological and Chemical Sciences, Birkbeck College, University of London, Malet Street, London WC1E 7HX
2. UCL Bone and mineral Centre Dept. of Medicine,London Centre for Nanotechnology, London.
3. British Museum Conservation Dept. Bloomsbury, London
4. Rapra Technology and formerly at X-At, Exeter Enterprises, University of Exeter, Exeter, Devon EX4 4RN

Introduction

Damage assessment of parchment is essential for its preservation. The physicochemical information can be used

(1) To provide informed advice about its state of degradation and to assist in developing appropriate conservation treatment.

During the EC-funded project 'Improved Damage Assessment of Parchment' (IDAP) a detailed database from accelerated aged (heat, light, moisture and pollutant gases) and historical samples (34) was established.

In this poster the data obtained from Dynamic Mechanical Analysis (DMA), Thermogravimetry (TGA), Attenuated Total Reflection - Fourier Transform Infrared Spectroscopy (ATR-FTIR),polarised microscopy and scanning probe techniques will be summarised.

Parchment and Parchment Degradation

Parchment is prepared from animal skin. The process involves dehairing, treatment in lime baths, and then drying under tension. Collagen is the main component of parchment and changes in its physicochemical state are of prime interest in this project.

Experimental Approach

Previous work on parchment assessment in terms of thermal stability and viscoelastic properties of the collagen polymer network was developed by our team in the framework of the EC funded MAP project [Odlyha et al. MAP]. This was extended in the IDAP project to include attenuated total reflection infra-red spectroscopy (ATR-FTIR) and scanning probe microscopes.

A. Effect of programmed RH on parchment

Testing load (0.05N) & RH linearly increasing (10-80% at 1%/min)

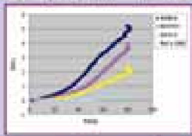

Figure 1 expansion (D%) vs RH (%) for control (black), control heated to 220°C (blue), Historical Florence binding (sheep) (previous water damage) (pink),School of Conservation binding (goat) (yellow)

Figure 2 Sample mounted in tensile mode

Table 1 : rate of expansion of parchment samples on humidification from the dehydrated state is given by Slope 1 (%/min). D(60%) & D (80%) are values for expansion at 60%RH &80% RH. Data for selected parchment samples (historical & accelerated aged) under load (0.05N) in head to tail direction are shown.

Sample		Slope 1	D60(%)	D80(%)
SC66.6	reference	0.0087	3.33	6.18
[illegible]	Historical Florence	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	reference	[illegible]	[illegible]	[illegible]
[illegible]	Historical Florence	[illegible]	[illegible]	[illegible]
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[illegible]	Historical Florence	[illegible]	[illegible]	[illegible]
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[illegible]	Historical Florence	[illegible]	[illegible]	[illegible]
[illegible]	School of Conservation	[illegible]	[illegible]	[illegible]
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[illegible]	School of Conservation	[illegible]	[illegible]	[illegible]
[illegible]	Historical Florence	[illegible]	[illegible]	[illegible]
[illegible]	Historical Florence	[illegible]	[illegible]	[illegible]
[illegible]	School of Conservation	[illegible]	[illegible]	[illegible]
[illegible]	School of Conservation	[illegible]	[illegible]	[illegible]
[illegible]	Historical Florence	[illegible]	[illegible]	[illegible]
[illegible]	School of Conservation	[illegible]	[illegible]	[illegible]
[illegible]	School of Conservation	[illegible]	[illegible]	[illegible]

Damage ranking

Green (1)

Yellow (2)

Orange (3)

red (4)

Acronyms for accelerated ageing are

(H) Heat 100°C,

(L)light ~ 17Mluxhrs)

Ranking of damage-rate of expansion compared to reference sample

(Slope 1) (calculated between 15-45mins i.e. between 20-40%RH).

Low rate suggests sample is apolar, crosslinked, and/or crystalline.

Observations Rate of expansion (moisture uptake) is dependent on sample history and pre-treatment of sample (accelerated ageing). Exposure to pollutant gases provides level of damage (in terms of response to RH) similar to that observed in some of the historical samples (Florence) and School of Conservation.

Heating reference sample to 220°C reduces rate of moisture uptake significantly. At nanoscale level corresponds to shrinkage of collagen fibrils (J.de Groot, private communication).

C. Polarisation Microscopy

Collagen is a birefringent and so modern parchment appears bright & gelatine appears dark between crossed polarisers

Figure 3. By recording one image between parallel polarisers and one image between crossed polarisers a damage distribution map can be calculated

Historical parchment

Figure 4 13th cent. Municipal Archive in Spain-concession of rights and privileges by Rey Alfonso X. ATR/FTIR ranked this example in damage category (2) and it coincides with ranking by polarisation microscopy & AFM

B. Atomic Force Microscopy

Figure 5 AFM image of the 13th century Segovian sample compared to an image of acc. aged parchment (32days 80°C & 40%RH). Green arrows point to intact areas, red arrows to areas with fibril swelling, orange arrows point to intermediate areas of damage.

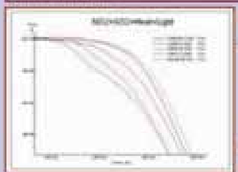
C. ATR-FTIR attenuated total reflection infra-red spectroscopy

Figure 6. Left ATR-FTIR spectra in amide I region showing reference (lower curve 1) and historical samples (upper curves 2). Right Figure 6 The distribution of samples ranked according to damage based on calculated ratios. (1) RH,T (2)pollutant (NO_x,mixed $NO_x SO_2$,heat and light (3)Nat.Archive of Scotland (4)School of Conservation DK (5) Archivio di Stato Firenze

The peak height **ratio** within amide I peak (**1660 cm^{-1} / 1630 cm^{-1}**) was used to evaluate damage based on previously reported work (Vyavahare, N.R *et al.*, 1998). Changes in this **ratio** suggest **degradation of the collagen triple helix structure**. The ratio was found to correlate to some extent with reduction in hydroxylysine content from amino acid analysis (School of Conservation) (Larsen et al.2005). Both are then measuring damage from mainly oxidative processes.

D. Oxidative Stability : Thermogravimetry (TGA)

Figure 7 (Left) TGA of mixed gas samples in temp. region 50-300C. Increase in damage with exposure (Right) Measure of wt. loss for pollutant gases and mixed gases



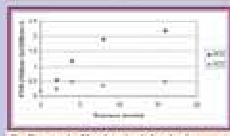


Figure 8 **left**: ATR/FTIR of polluted aged samples gives evidence of evolution of new peak at 1330cm^{-1} and can be monitored by the ratio 1330/1235 (cm^{-1}). Thus, changes occur more rapidly with NO_2 than SO_2

E. Dynamic Mechanical Analysis

are made using a sinusoidal load Thermal transitions which indicate that collagen is a viscoelastic polymer (Odlyha et al., 2002)

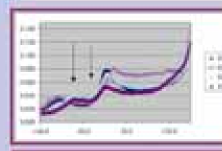


Fig 9 DMA peak at -40°C or at -60°C. Studies on polypeptides & dry proteins have shown that low T relaxations involve movements of side chains and T shift indicates ionic and polar side chains of the collagen molecule (Fois et al. 2000).

Acknowledgements

The authors are grateful to the European Commission DG-RTD 5th Framework "City of Tomorrow and Cultural Heritage" for funding the IDAP project (contract no. EVK4-CT-2001-00061). We also thank Victoria Smith (IDAP-subcontractor) for arranging sampling in Spain (Archivo Municipal de Segovia) and Nadia Smith for assistance with data processing.

. Micro-thermal analysis

Fig.10 Micro-thermal analysis uses a small probe with tip radius of 5 µm. This probe can be heated from 20 to 600°C Since the measurement area is only 5 by 5 µm, the damage to the parchment manuscript is minimal.

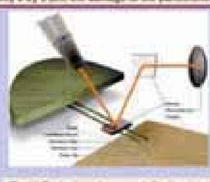
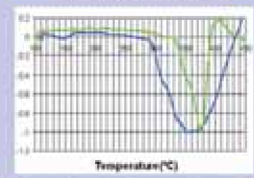


Fig 11 Derivative of sensor deflection (µm/s) vs T for rat tail collagen (green) and gelatin (blue)



E. Oxidative Stability : Thermogravimetry (TGA)

Thermogravimetry in an oxidising atmosphere provided information on (a) proportion of organic/inorganic content, b) more readily oxidised samples (implication that more polar and so react more readily in oxygen & degrade at lower T, c) crosslinked and/or crystalline/apolar (degradation at higher T)

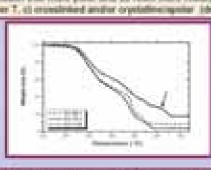


Figure 12 TGA curves (wt loss % vs T) are for reference (full line) and historical samples. Sample from National Archive of Scotland (top curve dot dash) has additional weight loss in region of 600°C due to calcium carbonate.

E. Quantification by derivative Thermogravimetry (DTGA)

Figure 13 (below left) DTGA curves (rate of wt loss % vs T) are for reference (red) and gelatin (dash). Broadening in gelatin compares with micro-thermal analysis. Effect of lipid presence is shown for historical sample (blue). Below right TGA and calculated DTG curves for control

Figure 14 DTGA was used to describe the degradation behaviour of historical samples using parameters (peak ratios and widths of 2nd peak)

Figure 15 TGA and DTGA curves are shown for historical samples (School of Conservation) (red and blue) and reference sample (black). SC75.2 (blue) and SC18 (red) show category 4 damage (Table 1). Both have low moisture response implying crosslinked and /or crystalline material, confirmed by higher peak ratios than the control.

SC18 has high lipids content (Ghioni et al.2005) and this makes it more apolar. SC75.2 has a large shift in the low temperature peak (DMTA), indicating presence of ionic and polar side chains of the collagen molecule. This explains why it is more readily oxidised than SC18, and that its degradation occurs at a lower temperature.

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<http://www.idap-parchment.dk/>

IDAP project (EVK4-CT2001-00061) with support from EC 5th Framework Programme, Key Action The City of Tomorrow and Cultural Heritage of the Energy, Environment and Sustainable Development Thematic Programme and the Danish Ministry of Culture.

Damage assessment of parchment: thermoanalytical (macro to nanoscale) and non-invasive spectroscopic analysis

M. Odlyha[1], C. Theodorakopoulos[1], J. de Groot[1,2], L. Bozec[2], M. Horton[2], Q. Wang[3], G.M. Foster[4] and R. Campana[1]

[1] School of Biological and Chemical Sciences, Birkbeck College, Bloomsbury, London
[2] UCL Bone and Mineral Centre, Dept. of Medicine & London Centre for Nanotechnology, London
[3] British Museum Conservation Dept. Bloomsbury, London
[4] Rapra Technology and formerly at X-At, Exeter Enterprises, University of Exeter, Devon

Key words: parchment, damage assessment, programmed RH, DMTA creep, ATR-FTIR, derivative TGA, micro-TA, AFM, ranking

Introduction and content

This paper is part of the European Project "Improved Damage Assessment of Parchment" (IDAP, Contract no. EVK4-2001-00061) [1]. The IDAP project provided the opportunity to develop and optimise methodologies for damage assessment and detailed descriptions of types of damage which would assist in performing appropriate conservation treatment. Markers of physicochemical change for model, model aged and historical samples were identified and this allowed classification of damage. This, together with the analytical data, was then entered into the DUPDA (Digitised User-friendly Parchment Damage Atlas) database. Previous work on parchment assessment in terms of thermal stability and viscoelastic properties of the collagen polymer network was developed by our team in the MAP project [2]. In the current project this was extended to include attenuated total reflection infra-red spectroscopy (ATR-FTIR) and scanning probe microscopy. The main objectives were to establish markers of change, initially for parchment samples subjected to cycles of accelerated ageing under controlled conditions, and to compare the results with actual damaged historical parchments and to rank damage.

European dimension

The IDAP project allowed collaboration with the National Library of the Czech Republic, Conservation Dept. An understanding was obtained of the methods of parchment preparation. Samples of prepared hides from various animals were also provided for testing. These samples, together with other model samples, provided a useful basis against which the wide range of model parchment samples subjected to controlled ageing using light, heat, elevated RH, and also pollutant gases (NO_2, SO_2, NO_2SO_2) alone and also with heat and light could be compared. Some collaboration was also instigated with the Municipal Archive in Segovia, Spain. Several visits were arranged where the damage assessment procedures were explained. They also provided an interesting sample from a 13th century document from a concession of rights and privileges made by Rey Alfonso X. Collaborative work was also taken up with some conservators-restorers in Germany who were eager to test polarisation microscopy as developed by one of our group for damage assessment.

Innovation and originality

Dynamic mechanical analysis (DMA), which had been used in the previous MAP project, included controlled environmental operation. This provided a damage classification in terms of sample response to moisture. DMA was also used to test the viscoelastic response of samples. These were frozen to liquid nitrogen temperatures and then heated slowly and a new observation was made. The first relaxation peaks occurred usually at low temperatures (about -80 ºC), after a preliminary heat to 150 ºC to bring samples to the same moisture content. However, for some samples, this peak was observed at higher temperatures (-40 ºC). The temperature at which the low temperature relaxation peaks occurred provided an indication of the type of side chains in

the collagen polymer network [3]. This has provided another marker for damage assessment and has been used together with other parameters.

Thermogravimetry monitors weight loss with temperature. It was found that pollutant ageing provided a weight change in the region of the curve between 150-300 ºC. This has not been observed in other accelerated aged samples or in historical samples and so appears as a marker for pollutant gas damage, in particular for NO_2. The weight change which occurs in the temperature region 400-530 °C provided further information on the state of the collagen network. Quantification of thermogravimetric (TGA) data of aged and un-aged parchments in this region was improved using the parameterisation approach. This provided markers for gelatinisation (increase in width of temperature range of degradation) which previously had not been detected. This correlated with broadening of transition as measured by micro-thermal analysis where gelatin was observed to degrade over a much broader temperature range than native (undenatured) collagen. Some historical samples showed a narrower temperature range of degradation and this was consistent with those containing lipid, as identified from ^{13}C solid state NMR spectroscopy. Further degradation beyond 550 ºC was observed in some historical samples and gave evidence of significant contributions from calcium carbonate. Residual inert material (up to 20%) remained after heating to 750 ºC in some of the historical samples. Additional measurements at selected heating rates and advanced data processing of the TGA data enabled calculation of kinetic parameters of degradation, and the prediction of thermal behaviour under isothermal and modulated temperature conditions [4].

In terms of structural information at the nanoscale level, the novel introduction of atomic force microscopy made it possible to record the periodic banding structure in the collagen of parchment (Figure 1). Furthermore an algorithm was written to quantify observed deviations from expected periodicity of banding. The frequency of distribution of deviations from expected values provided a classification of damage categories.

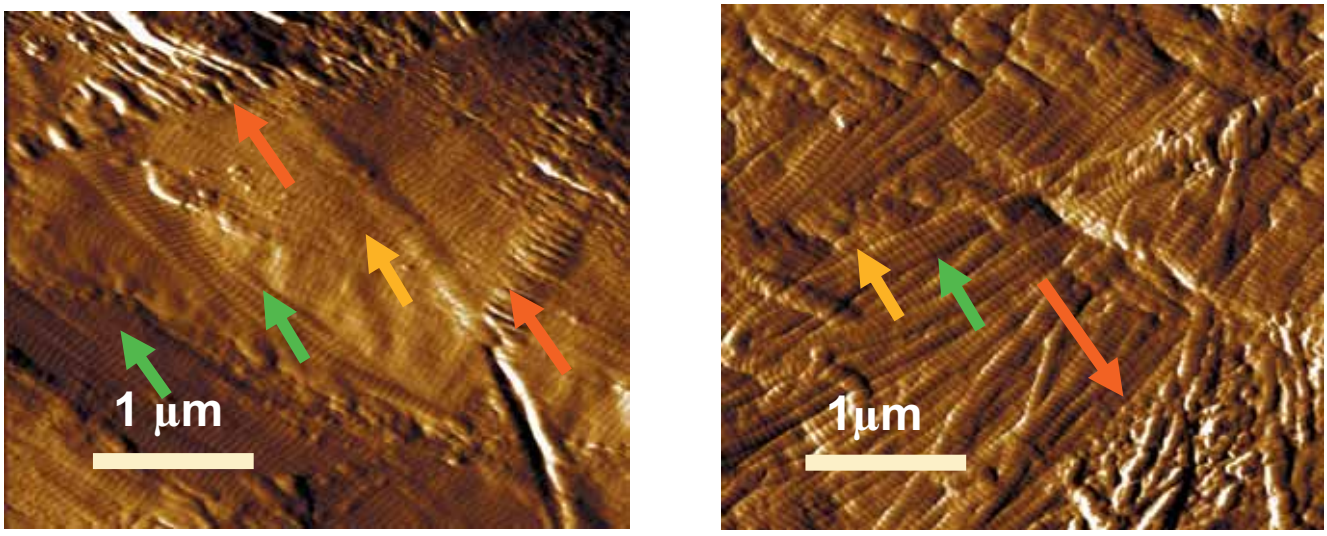

Figure 1: An AFM 'error' image of the 13th century Segovian sample (LHS) compared to an image of an accelerated aged parchment (80 °C and 40% RH for 32 days) (RHS). The green arrows point to intact areas, the red arrows to areas with fibril swelling, whereas the yellow arrows point to intermediate areas of damage.

Polarisation microscopy in transmitted light was also used to characterise the state of collagen. It was also considered a useful addition to the techniques as it is non-invasive. An algorithm was especially written to enable damage assessment from the superposition of images obtained in polarising and non-polarising light.

Attenuated total reflection infra-red spectrometry (ATR-FTIR) was used for surface chemical analysis. The peak height ratio within the amide I peak (1660 cm^{-1}/1630 cm^{-1}) was used to evaluate damage based on previously reported work [5]. Changes in this ratio suggest degradation of the collagen triple helix structure. The ratio was found to correlate to some extent with reduction in hydroxylysine content from amino acid analysis [6]. Both are then measures of damage from mainly oxidative processes.

Impacts

The approach developed in IDAP for quantification of damaged collagen by AFM has also been used by our medical colleagues for quantifying damage in collagen in bone. The study of viscoelastic properties of collagen is also of interest to polymer scientists. With regard to conservation, there is particular interest in the non-invasive testing using polarisation microscopy. This represents a simple and economical method accessible to conservators-restorers. Moreover the samples used in the IDAP project have also been characterised by a number of interdisciplinary techniques and this has left us with a very useful training set of samples. Several students, also from other European countries, have requested internships and access to these samples and the IDAP database.

Acknowledgement

The authors are grateful to the European Commission DG-RTD 5th Framework "City of Tomorrow and Cultural Heritage" for funding the IDAP project (contract no. EVK4-CT-2001-00061). We also thank Victoria Smith (IDAP-subcontractor) for arranging sampling in Spain (Archivo Municipal de Segovia) and Nadia Smith for assistance with data processing.

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[6] Larsen, R., Poulsen Vestergaard, D., Minddal, K., Fazlic, N., "Molecular Damage of Parchment studied by Amino Acid Analysis" (IDAP Workshop August,2005).

European project details

IDAP, Contract no. EVK4-2001-00061, Improved Damage Assessment of Parchment, René Larsen, The Royal Danish Academy of Fine Arts, School of Conservation, Esplanaden 34, DK-1263 Copenhagen C, Denmark.

Improved Damage Assessment of Parchment

The large collections of parchment documents in public and private libraries, archives and in Christian, Islamic and Jewish institutions etc., recognised as being among the most valuable objects of our European cultural heritage present an enormous, unsolved conservation problem.

Therefore, the objectives of the IDAP project were to assess damage to historical parchments at all structural levels from the macroscopic to the molecular in order to make available:

- A Parchment Damage Assessment Programme (PDAP)
- An Early Warning System (EWS)
- A Digitised User-friendly Parchment Damage Atlas (DUPDA)

These systems are now available on the Internet in the form of an interactive database which enable the end-users to improve communication and distribution of expertise and knowledge.

PDAP provides detailed information on new methods for identifying the condition of parchment to professional end-users, researchers and students working with practical parchment conservation and research.

PDAP consists of various simple visual, non-destructive and micro-sample assessment methods for routine damage assessment of parchment on the macro-level (visual and microscopic) including an assessment manual, report scheme and search facilities.

The methods and techniques have been supported by the results of correlation analyses between the results from advanced chemical, structural and thermo-chemical studies of parchment deterioration from the microscopic to the molecular level.

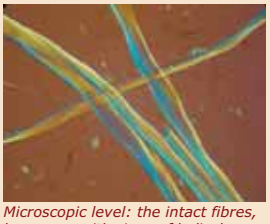
DUPDA describes the progressing damage of parchment in four categories of damage, evolving from the intact to the heavily damaged at all structural levels as detected by the various assessment and analytical techniques.

The IDAP database also provides other facilities like detailed description of the analytical techniques used, typology of damage of the parchment and general recommendations and precautions in connection with storage, exhibition and treatment of parchment

The coordination and organisation take place within the framework the non profit IDAP Network.

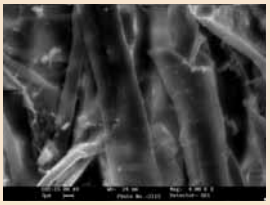
New intact parchment visualised at different structural levels

Damaged historic parchment visualised at different structural levels.

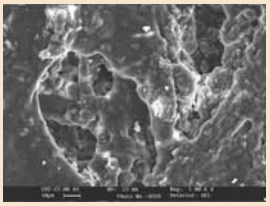


Microscopic level: the intact fibres, long even with signs of helical twisting

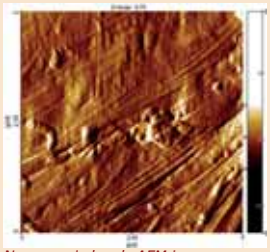
Microscopic level: Deteriorated fibres partly flat, shrunken and cracked.



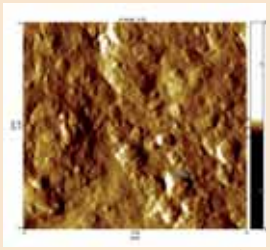
Mesoscopic level: SEM image showing intact elementary fibres



Mesoscopic level: SEM image showing melt like aspects with surface cracks, swollen elementary fibres and breaks.

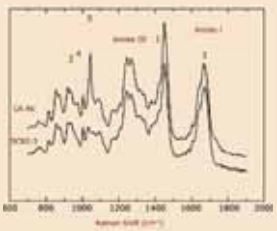


Nanoscopic level: AFM image, surface of micro fibrils. Structure and the axial repeat are visible.



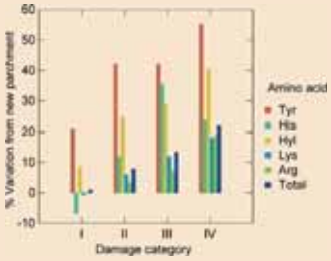
Nanoscopic level: AFM image, surface of micro fibrils. Loss of a micro fibril structure and axial repeat.

Assessment on the molecular level



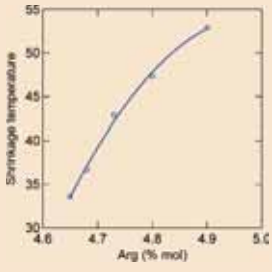
Classification of samples into damage categories according to the Raman spectra.

Group/category	1. No or very small changes	2. Minor changes	3. Medium changes	4. Major changes
Occurring signatures in Raman spectra	none	1, 3	1, 2, 3	1, 2, 3, 4, 5

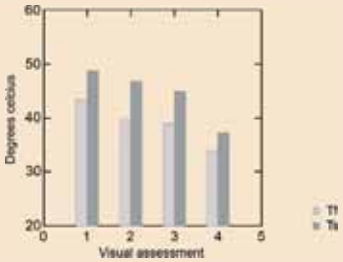


Amino acid analyses - classification into damage categories according to changes in the amino acid profile of historic parchments.

Relations between assessment data of historic parchments



Microscopic and molecular: Shrinkage temperature (Ts) vs. Arginin. Using function: $Ts = \beta_1 Arg^2 + \beta_0$, a correlation coefficient of 0.9831 is obtained.



Micro- and macroscopic: Mean of first observed shrinkage Tf and the shrinkage temperature Ts of samples in the 4 damage categories given by visual assessment.

Contractors in the IDAP project:

The Royal Danish Academy of Fine Arts, School of Conservation, Copenhagen, Denmark
FORTH/ICE-HT and Department of Chemical Engineering, University of Patras, Greece
Birkbeck College, University of London, United Kingdom
Centre de Recherches sur la Conservation des Documents Graphiques, CRCDG, Paris, France
Department of Optometry and Vision Sciences, University of Cardiff, United Kingdom
Department of Chemistry IFM, University of Torino, Italy
The Royal Library, Copenhagen, Denmark
The National Library of the Czech Republic, Prague, the Czech Republic

Subcontractors and end-user partners in the IDAP project:

Section of Biochemistry and Nutrition (B&E), Technical University of Denmark
Department of Food Science and Microbiology (DISTAM), University of Milan, Italy
National Archives of Sweden
National Archives, United Kingdom
Archivio di Stato di Torino, Italy
Archivio Storico della Città di Torino, Italy
The Archives of Prague Castle, the Czech Republic
Archivo Muncipal de Segovia, Spain

www.idap-parchment.dk

IDAP project (EVK4-CT2001-00061) with support from EC 5th Framework Programme, Key Action The City of Tomorrow and Cultural Heritage of the Energy, Environment and Sustainable Development Thematic Programme and the Danish Ministry of Culture.

Improved damage assessment of parchment

René Larsen

The Royal Danish Academy of Fine Arts, School of Conservation, Denmark

Key words: parchment, damage assessment programme, database, structural levels, end-users

Introduction and content

The background for the project are the large collections of parchment documents in public and private libraries, archives and religious institutions etc. which are recognised as being among the most valuable objects of our European cultural heritage. These documents present an enormous, unsolved conservation problem. No standard methods for assessment of damages as well as detailed descriptions of the damage types and causes existed to help in planning and execution conservation actions. Moreover, the general lack of resources and scientific data on deterioration from analysis and assessment of original historic parchments hindered the development of research and knowledge. Therefore, the main objectives of the IDAP project to overcome the above-mentioned problems were to make the following tools available for professionals on the Internet [1, 2]:

- A Parchment Damage Assessment Programme (PDAP)
- An Early Warning System (EWS)
- A Digitised User-friendly Parchment Damage Atlas (DUPDA)

The development of the simple and visual assessment techniques and the improvement of the knowledge on damage of parchment have been based on analysis and description of the damage characteristics on all structural levels from the macroscopic to the molecular [3]. The assessment methods and techniques in PDAP have been developed in close cooperation with end-users at archives and libraries in Europe. They have been involved in the development, description and evaluation of the methods and actively involved in producing assessment data and knowledge essential for the development of DUPDA and EWS.

Figure 1: The IDAP assessment programme was developed in close cooperation with end-users in Europe, trained in workshops and used by the project partners and end-user to produce assessment data for the project research and development

The PDAP consists of various simple visual, non-destructive and micro-sample assessment methods for routine damage assessment of parchment on the macro level (visual and microscopic). The programme includes an assessment report scheme, descriptions and guidelines for performing the tests and reporting. The damage atlas (DUPDA) describes the progressing damage of parchment in four categories of damage, evolving from the intact to the heavily damaged at all structural levels. DUPDA also provides new general recommendations and precautions in connection with storage, exhibition and treatment of parchment in each of the four damage categories. In addition, the model early warning system (EWS) based on parchment sensors are suggested to warn against damage to historic parchment in storage and exhibition.

European dimension

The salvation of serious problem of preservation the invaluable parchment documents and artefacts has been hindered by the lack of detailed knowledge on their deterioration and proven standardised methods of damage assessment. The IDAP damage assessment contributes to extending the lifetime of and the access of these documents and so contributes to policy at the European level (Theme 2.4.1 City of Tomorrow and Cultural Heritage of the 5th Framework Programme). The potential for the transfer of the project results are good, and started already during the project. The IDAP project strategy and continuous activities will contribute to bridging the gap between researchers and practitioners. The IDAP database enables the end-users to improve communication and distribution of expertise and knowledge within conservation in the European Community and worldwide and the IDAP network will continuously present and publish the ongoing development and results of the assessment and research in relevant international journals and conferences and the IDAP researchers will continuo to offer end-user institutions to train individual experts in the techniques In addition, IDAP workshops are planned to be held regularly in the future. These workshops are very valuable in the way that conservators are taught to perform visual assessment on parchment in the same standardised way.

Innovation and originality

The main output of the IDAP project is the non-profit interactive parchment database, available on the Internet, containing the PDAP, EWS and DUPDA which are available for the work and progress in practical applied parchment conservation, education and research as well as in other relevant fields like biochemistry, protein chemistry etc. The products in the form of PDAP, User Guide, DUPDA and the many other website facilities constitute new and unique tools in practical damage assessment, storage and conservation of parchment. The output also includes the new and improved knowledge, expertise and developed analytical techniques that will be channelled into development and research in conservation and materials of parchment and other related materials. In addition, the results of the extensive analytical programme demonstrate the fact that it is necessary to thoroughly investigate objects at more than one level.

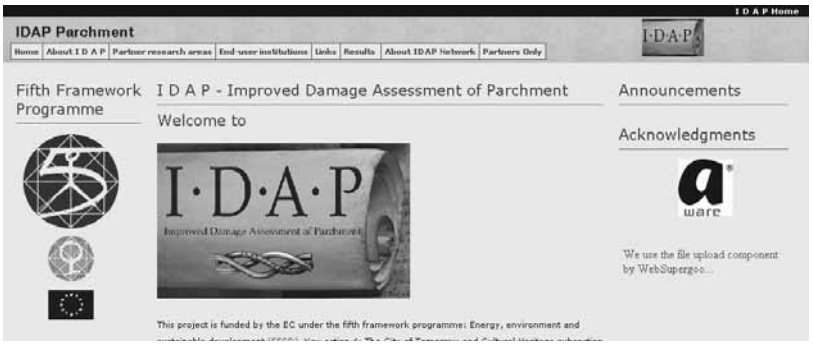


Figure 2: Front page of the IDAP website

Impacts

In general, the resources available for research in assessment and conservation of parchment documents are very limited. The availability of a parchment damage assessment programme on the internet is a solution to the problem of lacking resources and provides new and better standardised tools for damage assessment. The unique, interactive IDAP database and its facilities, create the possibility of uniting the existing and new research and practical conservation knowledge. Moreover, it may contribute to improving communication and dissemination of expertise and knowledge within conservation in the European Community. The IDAP methods and facilities enables the end-users to set up selective, strategic conservation plans and actions and thus avoid excessive waste of resources expenditure (financial, working hours etc.) or even to avoid efforts expended on useless, non-effective or, in worst case, damaging preservation actions. These improve the possibilities of extending the lifetime of the large number of invaluable parchment documents and artefacts and the possibilities of the access of the public to these. The IDAP system is already in use in assessment of collections as well as in the assessment of some very important unique parchment manuscripts and artefacts and introduced in conservation-restoration education programmes in Europe. Together these will consolidate and increase the leading position of European research and conservation of parchment.

Acknowledgement

The IDAP project partners are grateful to the European Commission DG RTD and the Danish Ministry of Culture for the financial support; to Section of Bio-chemistry and Nutrition (B&E), Technical University of Denmark and Department of Food Science and Microbiology (DISTAM), University of Milan, for supplying analyses and expertise; to National Archives of Sweden; National Archives, United Kingdom; Archivio di Stato di Torino, Italy; Archivio Storico della Cittá di Torino, Italy and The Archives of Prague Castle, the Czech Republic for invaluable contribution to the development of the assessment programme and providing assessment data and samples. Thank to Michel Chapuis, European Commission DG RTD – I.5 – "The City of Tomorrow and Cultural Heritage" for help in project administration; to Karen Borchersen and Jytte Grønlund for administrative and practical assistance and to Christina Lund, School of Conservation, for proof-reading manuscripts.

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European project details

IDAP, Contract no. EVK4-2001-00061, Improved Damage Assessment of Parchment, René Larsen, The Royal Danish Academy of Fine Arts, School of Conservation, Esplanaden 34, DK-1263 Copenhagen C, Denmark.

PAPERTREAT
PRESERVING PAPER-BASED COLLECTIONS

Jana Kolar[1], Matija Strlic[2], Tomasz Lojewski[3], John Havermans[4], Ted Steemers[5], Barry Knight[6], Jonas Palm[7], Jozef Hanus[8], Olga Perminova[9], Thi-Phoung Nguyen[10], Henk Porck[11], Yola de Lussenet[12]

1. National and University Library of Slovenia, Slovenia, **2.** University of Ljubljana, Slovenia, **3.** Jagiellonian University, Poland, **4.** TNO, The Netherlands, **5.** Het Nationaal Archief, The Netherlands, **6.** The British Library, United Kingdom, **7.** Riksarkivet, Sweden, **8.** Slovenský národný archív, Slovakia, **9.** Russian state library, Russian Federation, **10.** Bibliotheque nationale de France, France, **11.** Koninklijke bibliotheek, The Netherlands, **12.** ECPA, The Netherlands

The memory of civilisation is inherently linked to the written word which, written on durable materials, withstood the test of time. For more than five centuries, paper has been the predominant carrier of information and numerous medieval manuscripts bear witness of its durability. Changes in the quality of its production introduced in the 19th century, however, have dramatically reduced its lifetime, leaving devastating effects on the library and archival holdings. Condition surveys have revealed that one out of four books can no longer be used due to the brittleness of paper, while additional 60% is endangered by acids.

In order to prolong the usable time of the vast quantities of original materials, paper collections may be treated with alkalies and/or stored at appropriate conditions. While preservation options are known, lack of the competent comparative studies still leaves collection keepers hesitant of their use.

Within PaperTreat project, several European libraries and archives have joined forces with the top research laboratories to provide information on the extension of the usable life of paper, as achieved by mass conservation treatments as well as storage at low temperatures, to identify the side effects of the treatments and to provide the cost specification for each treatment. In addition, the project will develop standard model materials, evaluation criteria and quality control criteria, which will considerably simplify evaluation of the emerging new technologies.

PaperTreat project will enable development of the most cost-effective preservation strategies for the decaying collections and thus assure safekeeping and long term access to the endangered written cultural heritage.

The impact assessment study of the project's results will be conducted at the end of the project, which will contribute to a formation of a sounder base for investment and policy decisions regarding cultural heritage research.

Project webpage
http://www.science4heritage.org/papertreat/

European Project Details
PaperTreat: SSPI-006584
Evaluation of mass deacidification processes.
Coordinator: Jana Kolar,
National and university library, Slovenia,
e-mail: jana.kolar@nuk.uni-lj.si

Acknowledgement

PaperTreat project – preserving our paper-based collections

Jana Kolar[1], Matija Strlič[2], Tomasz Lojewski[3], John Havermans[4], Ted Steemers[5], Barry Knight[6], Jonas Palm[7], Jozef Hanus[8], Olga Perminova[9], Thi-Phoung Nguyen[10], Henk Porck[11] and Yola de Lussenet[12]

[1] National and University Library of Slovenia, Ljubljana, Slovenia
[2] University of Ljubljana, Ljubljana, Slovenia
[3] Jagiellonian University, Krakow, Poland
[4] TNO, Delft, The Netherlands
[5] Het Nationaal Archief, Den Hague, The Netherlands
[6] The British Library, London, United Kingdom
[7] Riksarkivet, Stockholm, Sweden
[8] Slovenský národný archív, Bratislava, Slovakia
[9] Russian state library, Moscow, Russian Federation
[10] Bibliotheque nationale de France, Bussy-Saint-Georges, France
[11] Koninklijke bibliotheek, Den Haag, The Netherlands
[12] ECPA, Amsterdam, The Netherlands

Key words: cultural heritage on paper, mass deacidification, preservation

Introduction

Changes in production technology in 19th century caused a shift of pH of paper to acidic regions, which resulted in a massive decay of library and archival holdings. Although the preservation strategies- mass deacidification and storage at low temperatures are well known, their effect on the real-time ageing has not been established. In addition to the evaluation of side effects and cost estimates, this data is essential for the development of a suitable preservation strategy.

The main objectives of PaperTreat project are to provide information on the extension of the usable life of paper, as achieved by mass conservation treatments as well as storage at low temperatures, to identify the side effects of the treatments and to provide the cost specification for each treatment. In addition, the project will develop standard model materials, evaluation criteria and quality control criteria, which will considerably simplify evaluation of the emerging new technologies.

European dimension

More than 150 years of use of the acidic sizing technology have left devastating effects on the library and archival holdings. Condition surveys have revealed that one out of four books can no longer be used due to the brittleness of paper, while additional 60% is endangered by acids.

In an attempt to remedy the situation, mass conservation processes, which neutralize the acids with the use of alkalies, were developed. Several European countries have undertaken comparative examinations of these systems within the past two decades, yet the high cost associated with such studies and the lack of the necessary instrumentation and expertise, limited the scope of the studies. So far, no data on the extension of useful life of the acidic paper at room temperature, as a result of mass deacidification was provided, leaving libraries and archives hesitant of its use.

Within PaperTreat project, several European libraries and archives have joined forces with the top research laboratories to provide the data, which will enable them to develop the most cost/efficient preservation programmes. This will assure safekeeping and the long term access to the endangered written cultural heritage.

Innovation and originality

Within the PaperTreat project, the state of the art analytical methodologies will be used, while several new ones will have to be developed, in order to provide reliable with a minimal damage to the originals. Results obtained with near infrared spectroscopy, developed within another running 6th framework project SurveNIR (www.science4heritage.org/surveNIR), as well as two recently completed 5th framework projects Papylum and InkCor will be integrated as well.

The approach will enable determination of the stability of the endangered materials at room temperature, which will allow estimation of rate of decay of the collection, as well as the effects of the preservation measures. In addition, the methodology, including model materials will be standardised.

As part of the dissemination strategy, a workshop will be organised in spring 2008, accompanied by a booklet on best strategies for preservation of endangered written cultural heritage.

Impacts

The project supports EU policies which stress the importance of preserving and enhancing cultural heritage. Through evaluating the environmental and health aspects of the deacidification techniques, the project will contribute to healthier environment. Enhanced preservation of cultural heritage, as a result of PaperTreat project may also be considered as an important indirect economic investment. Keeping in mind that the costs of the decay of European cultural heritage are estimated at more than 14 billion Euro per annum, the improved methods for preservation of paper based cultural heritage developed through PaperTreat will also enable better use of existing resources.

The impact assessment study of the project's results will be conducted at the end of the project, which will contribute to a formation of a sounder base for investment and policy decisions regarding cultural heritage research.

European project details

PaperTreat
SSPI-006584 Evaluation of mass deacidification processes.
Coordinator: Jana Kolar, National and university of Ljubljana, Slovenia, e-mail: jana.kolar@nuk.uni-lj.si
Project webpage
http://www.science4heritage.org/papertreat/

ASSESSMENT OF MICROBIOLOGICAL DETERIORATION OF PARCHMENT USING SIMPLE VISUAL METHODS

Magda Součková
National Library of the Czech Republic, Czech Republic

The work has been accomplished within the scope of the three-year international research programme „Improved Damage Assessment of Parchment“ (abbreviated as „IDAP“)

Task of the research

Inducing an artificial microbiological deterioration of parchment and describing its symptoms in the light of the simple visual assessment in agreement with the IDAP parchment assessment report.

Microbiological deterioration of parchment?


See at the bottom.


Goat

Parchments used

Goat and sheep parchments produced in the restoration department of the NLCR according to the medieval technology.


Sheep

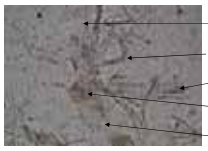
Details of used simple non destructive techniques of the assessment of the parchment damage

Microscopic analyses of wet fibres (microscope magnification 200x)

The major constituent of parchment is a protein collagen type I. Left handed elementary fibres (diameter of about 1000 nm) are visible in a light microscope. The ageing and overall degradation of parchment reflect on the state of the collagen fibres. In the IDAP project different kinds of fibres degradation were described: appearance of short fibres and many fragments, splitting, fraying, cracks, gelatinisation. Preparing of fibres samples: parchment defibering in distilled water with a scalpel or preparation needles.

Kinds of fibres degradation


Non-damaged fibres



Damaged fibres

Stages of microbiological deterioration of fibres samples

Slight


Long fibres,some splitting and fraying

Advanced


Shorter fibres ,splitting, fraying and cracks,a lot of fragments,partially gelatinized

Heavy


Fibres sample totally gelatinized and fragile

Determination of hydrothermal stability (shrinkage temperature,Ts) of collagen materials by the micro hot table technique (microscope magnificatiion 40x)

When collagen fibres are heated in water they will deform over a distinct temperature interval.The deformation is apparent as a shrinkage of the fibres. Ts=the temperature when at least two fibres show shrinkage activity simultaneously and continuously.


Before heating


Ts = 45,9 °C

First series of experimentation

Micro-organisms: Actinomycetes, Bacteria, mixture of moulds

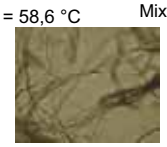
Conditions of artificial microbiological deterioration: Actinomycetes – putting the parchment in the leaf-mould, 22ºC;Bacteria (Bacillus subtilis) – putting the parchment in the aqueous medium, 22ºC;Mixture of moulds – putting the parchment in the environment of 100% RH, 22ºC.

Tested properties: surface and its appearance, microscopy of fibres, shrinkage temperature (micro hot table method).

Actinomycetes,28 days,Ts= 57,4 °C


Bacteria,3 months, Ts = 62,7 °C


Ts = 58,6 °C



Mixture of fungi, 100% RH, 6 months

melted

Second series of experimentation:

Micro-organisms: Aspergillus flavus, Aspergillus versicolor, Aspergillus niger, Penicillium chrysogenum, Penicillium expansum, Cladosporium cladosporoides, Scopulariopsis brevicaulis.

Conditions of artificial microbiological deterioration: The parchment samples were sterilized, inoculated with pure fungi cultures and cultivated on the incomplete Czapek-Dox agar without the source of carbon , in the environment of 100%RH and on the complete Czapek-dox agar - only in the case of goat parchment, all done in the thermostat at 25ºC.The parchment samples were taken subsequently in 4 to 153 days after inoculation. The samples were photographed, the mould washed up, the parchments dried and photographed again. Then they have been kept in a dry state.

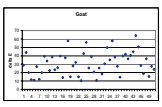
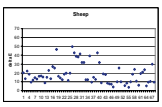
Properties under examination: thickness, colour, surface and its appearance, microscopy of fibres, shrinkage temperature (micro hot table method).

Thickness: Changes in thickness happen in almost 100% cases of microbiological deterioration and are very large – up to 50% over the original. After a microbial artificial ageing larger changes in thickness were found on goat parchments than on sheep parchments. However, the variability of parchment thickness is due to its hand manufacture and for that reason cannot be used for microbiological deterioration identification.

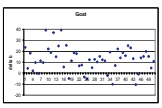
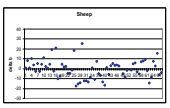
Colour: A microbiological attack on parchment causes always a visible change of colour. The biggest proportion of colour difference ΔE falls on darkening or yellowing. Goat parchments show greater changes in colour than sheet parchments. Owing to microbiological deterioration sheet parchments tend to blueing.

Color space L*a*b*

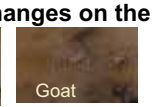
Changes of colour - ΔE

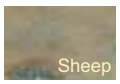



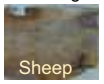
Changes of colour - Δb

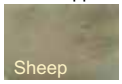
Visible changes on the parchment surface: After the microbiological ageing several kinds of changes were apparent on the parchment surface.


Sheep

Goat
Protuberances


Goat

Sheep
Cracks


Sheep


Goat
Decrease of mass


Sheep
Loss of the grain layer


Goat

Goat
Circle holes

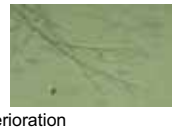
Shrinkage temperature: The maximum drop of shrinkage temperature for both kinds of parchments is similar – 10% for goat parchments and 12% for sheep parchments – with the exception of totally degradated zones. The collagen fibres in these parts are melted and are not shrinking any more.

Identification of microbiological parchment damage



Microbiological deterioration

Change of colour
Crack of grain side
Splitting of fibres



Non-microbiological deterioration

Change of colour
Loss of grain layer
Non-damaged fibres

European Project Details
Contract number : EVK4-CT-2001-00061
Title of the Project: Improved Damage Assessment of Parchment - IDAP“
Co-ordinator: Dr. René Larsen, **School of Conservation, The Royal Danish Academy of Fine Arts** , Copenhagen, Denmark,rl@kons.dk

Assessment of microbiological deterioration of parchment using simple visual methods

Magda Součková

National Library of the Czech Republic, Czech Republic

Key words: microbiological deterioration, fungi, parchment, fibres, microscope, shrinkage temperature

Introduction and content

Between 2002 and 2005, a three-year international research programme "Improved Damage Assessment of Parchment" (abbreviated as "IDAP")[1] has been launched and the Restoration Department of the Czech Republic participated in tackling the problem. One of the special tasks accomplished in the Czech Republic dealt with the microbiological deterioration of parchment in connection with using of simple non destructive techniques of the assessment of the parchment damage. There is not a single valued identification of microbiological parchment damage in all cases, mainly in the early stage. Therefore an artificial microbiological deterioration of parchment has been induced and its symptoms described in the light of the simple visual assessment in agreement with the methodology used in the IDAP project. It has been stated that the salient features of the microbiological parchment deterioration include change of colour and creation of colour stains, longitudinal splitting of collagen fibres perceptible in the light microscope, and in an advanced stage of degradation decrease of the parchment mass.

European dimensions

In the IDAP research project the original methodology of simple visual assessment of parchment has been elaborated which can be applied with basic equipment in conservation workshops. Being applied to identify and assess the microbiological degradation of parchment, especially as far as microscopical assessment of fibres is concerned, it will enable discovering microbiological deterioration even in early stages or in the cases when no rests of microbiological bodies remained on the parchment.

Innovation and originality

Two series of experimentation have been done. In the first series an artificial ageing of parchment was induced through the action of Actinomycetes, Bacteria and mixtures of fungi. Seven species of the most represented fungi were chosen according to the microbiological research of the Codex of Vysehrad made in the National Library in 1991 for the second series of experimentation which were done with two kinds of parchments (goat and sheep). Having been inoculated by pure moulds cultures, the parchment samples were subsequently tested after 4 to 153 days of cultivation. Their appearance was registered, both with the mould and after the mould was removed. The changes of chosen properties were observed on the parchments in dry state: thickness, colour, transmission, appearance of the parchment surface, microscopy of fibres, shrinkage temperature (micro hot table method) [2]. The changes caused by microorganisms on goat and on sheep parchments were compared. Among the mentioned tested properties the following changes seem to be the most characteristic for the microbiological deterioration: colour changes, loss of the parchment mass and the changes of collagen fibres

observable under microscope. The microbiological attack on parchment causes always a visible change of colour. The biggest proportion of colour difference ΔE falls on darkening or yellowing. Owing to microbiological deterioration sheet parchments tend to blueing. On the parchments surface after the microbiological ageing several kinds of changes were observable: protuberances, cracks of the grain side, embrittlement of the parchment and loss of the mass, circle holes and loss of the grain side. The fibres of parchments after a slight microbiological damage are long with some splitting and fraying. The sample of parchment fibres in an advanced stage of microbiological deterioration contains shorter fibres with splitting, fraying and cracks and many fragments, some of them partially gelatinized. Fibres samples of parchments heavily damaged by microbiological deterioration are melted or totally gelatinized. The maximum drop of shrinkage temperature for both kinds of parchments is similar – 10% for goat parchment and 12% for sheep parchment – with the exception of totally degradated zones. The collagen fibres in those parts are gelatinized and are not shrinking any more. Macrophotographs of parchments after the microbial ageing and microphotographs of fibres were put together in two atlases "Microbiological deterioration of goat parchment" and "Microbiological deterioration of sheep parchment", to become accessible on the IDAP web pages.

Impact

Taking care of cultural heritage in view to save it for the future generations it is of cardinal importance to know in detail the real physical state of the objects. An analysis of the kind and degree of deterioration is crucial for the restorer to make the decision of the type of preservation or saving of the object.

Acknowledgement

We wish to express our thanks to Dr René Larsen from the School of Conservation in Copenhagen for his courtesy in allowing us to take part in the project and for his assistance during the research.

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European project details

IDAP – Improved Damage Assessment of Parchment

Contract number: EVK4-CT-2001-00061

Co-ordinator: Dr. René Larsen, School of Conservation, The Royal Danish Academy of Fine Arts, Copenhagen, Denmark

ANALYSIS OF PARCHMENT BOOKBINDINGS BY INFRARED THERMOGRAPHY

F.Mercuri, F.Scudieri, S.Paoloni, M.Marinelli, U.Zammit

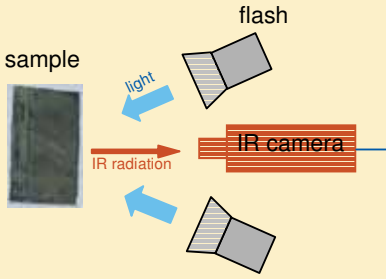
Università di Roma "Tor Vergata" - Dipartimento di Ingegneria Meccanica and Laboratorio METER della Facoltà di Lettere e Filosofia

INFRARED THERMOGRAPHY

Infrared Thermography is based on the analysis of the heat diffusion in a sample. Here a new application of this method to the study of historical bookbindings and to the investigation of one of their most used component, the parchment, is presented.

It provides information on many aspects such as:

1. Sub-surface structure of parchment bookbindings and parchment inhomogeneities
2. Fibres network microstructure of the parchment and ageing effects
3. Damages by the combined effect of ageing and ink



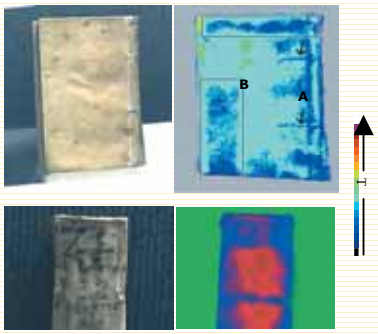
SET-UP

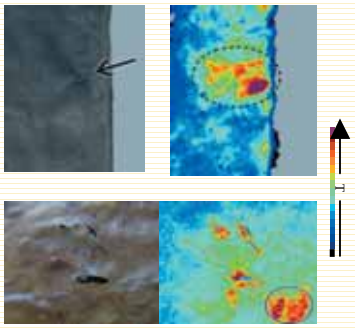
An infrared camera is the basic element of the thermographic set-up. It records temperature maps (thermograms) of the sample surface which cools down following pulsed heating produced by light absorption.

1 Thermograms

Parchment bindings: sub-surface structure

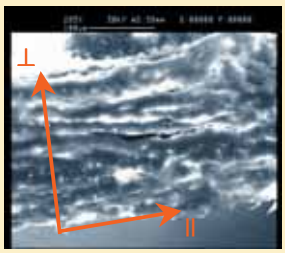
Parchment deteriorated areas and inhomogeneities





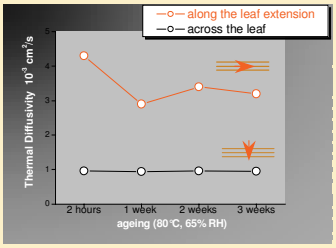
2 Parchment anisotropy

Parchment has a layered anisotropic structure which is reflected in anisotropy of the heat diffusion properties. Deterioration associated with ageing reduces the anisotropy of the parchment.



Thermal diffusivity and deterioration

This aspect has been pointed out by mean of thermal diffusivity measurements, via thermography (non-destructive and non-contact) to quantitatively monitor particular types of microstructural deterioration processes in the parchment

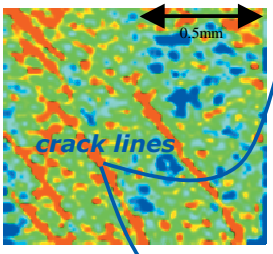


3 IR Thermography and damage mapping

Modern parchment leaf cross-section, inked on the upper side and artificially aged 3 weeks at T=80°C and RH=65%.

Extended detachments have been produced just below the upper inked surface ending with a crack line.

Such kind of subsurface damages are spread below the entire inked surface and shown as peculiar (red) striped features by the thermogram which represents a global map of the subsurface damage distribution.



Analysis of parchment bookbindings by infrared thermography

Fulvio Mercuri, Folco Scudieri, Stefano Paoloni, Ugo Zammit and Massimo Marinelli

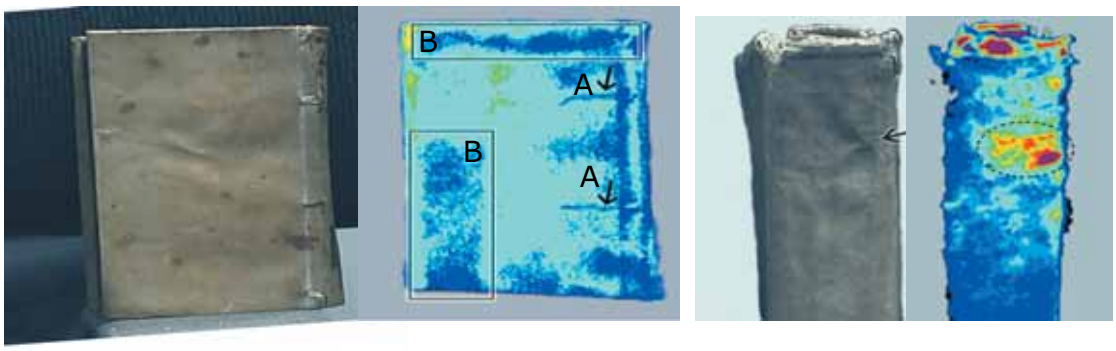
Dipartimento di Ingegneria Meccanica and Laboratorio di Metodi e Tecnologie per il Restauro dei Beni Librari, Facoltà di Lettere e Filosofia – Università di Roma "Tor Vergata", Via del Politecnico 1, 00133 Roma, Italia

Key words: parchment, thermography, thermal properties

Introduction and content

Infrared thermography diagnostics has been applied to the study of ancient bookbindings and to the analysis of one of their most common component material, the parchment. By mean of the thermographic method, it was possible to analyse the bookbinding structure and detect the presence of damage, which could not be detected by optical or mechanical analysis, to test the adhesion state of the different parts of the bindings and to investigate the techniques employed for the assembly of the different binding components [1]. Moreover, thermal transport properties of artificially aged modern parchment have been studied and related to the microstructure features of the samples. The heat diffusion process has been shown to be direction dependent so reflecting the anisotropic nature of the parchment structure. Such an anisotropy become smaller with ageing and can be selected as a feature for evaluating deterioration. Finally micro damages in the *cross-section* layered structure, originated by ageing in previously inked parchment leaves, has been also described.

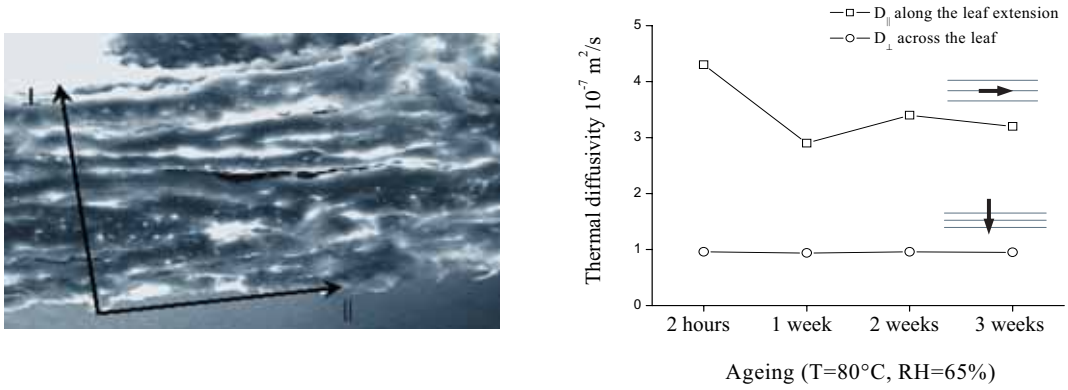
Concerning the analysis of the bookbinding structure, thermography provides false colour maps of the artefact, the so called thermograms, showing some of its subsurface features or inhomogeneities of the material [2]. In Figure 1a the image and the corresponding thermogram of a 17th century volume with limp parchment cover is reported. The thermogram reveals the contact areas (B) between external cover and turn-in shows and the hidden paths (A) of the sewing supports.



a b

Figure 1: a) A 17th- century volume with limp parchment cover. The thermogram reveals the contact areas B between external cover and turn-in shows and the hidden paths A of the sewing supports. b) The back of a 18th century hardback parchment binding. The arrow indicates a tear in the parchment while the corresponding thermogram indicates an area immediately surrounding the tear in which the density of the tissue is lower

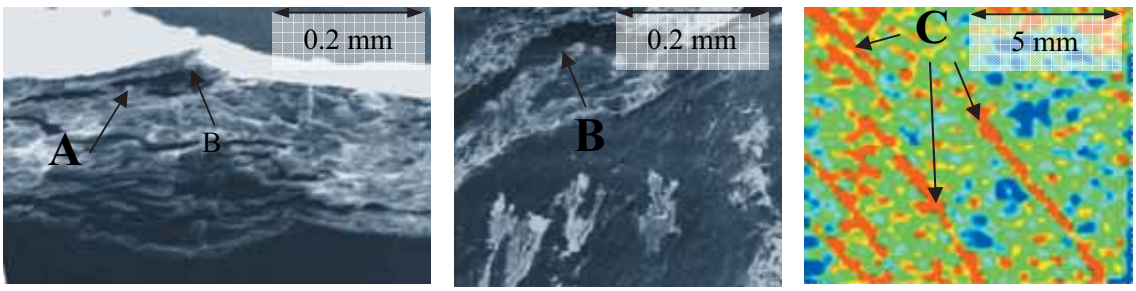
Figure 1b regards the back of a 18th century hardback parchment binding. The arrow indicates a tear in the parchment while the corresponding thermogram indicates an area immediately surrounding the tear in which the density of the tissue is lower. As mentioned above, thermography also provides a method to study the thermal transport properties and to measure one of the thermal transport parameters, the thermal diffusivity (D), for different directions inside the sample. Due to the peculiar anisotropic structure of the parchment (see Figure 2a) the thermal diffusivity has been measured along both the direction perpendicular ($\perp$) and parallel ($\parallel$) to the parchment leaf plane as a function of ageing. The obtained results are summarized in the plot of Figure 2b.



a b

Figure 2: a) parchment leaf cross-section obtained by SEM (Scanning Electron Microscopy). The arrows represent the two investigated heat diffusion directions. b) Thermal diffusivity values measured across ($\perp$) and along ($\parallel$) the parchment leaf as a function of the ageing time

For all the investigated samples the thermal diffusivity values $D_\perp$ measured across the parchment leaf are smaller than the $D_\parallel$ ones obtained for the in plane heat diffusion reflecting the anisotropic nature of the parchment structure. The sample ageing does not seem to significantly affect the $D_\perp$ value while a decrease of the $D_\parallel$ value was observed that the authors relates to a transformation in the building units of the *in-plane* fibres structure [3]. The above described thermal anisotropy is also observed in all the (elsewhere) studied samples of deteriorated historical parchment. For that kind of samples however the anisotropy was less relevant suggesting that the deterioration processes make some parchment features progressively more isotropic. We have finally characterized a particular kind of damage induced into the parchment microstructure by the combined action of ink and ageing.



a b c

Figure 3: a) SEM cross-section of the parchment leaf: the inked surface is the upper one. b) SEM top view of the inked surface. c) Thermogram of the inked surface: white slanting stripes correspond to the detachment paths under the inked surface along the crack lines

In Figure 3a an image of a modern parchment leaf cross-section, inked on the upper side and artificially aged 3 weeks at T = 80 °C and RH = 65%, is reported. The image shows an extended detachment (A) just below the upper inked surface ending with a crack line (B) which is also visible from the top view reported in Figure 3b. Such kind of subsurface damages are spread below the entire observed inked area as shown by the thermogram in figure 3c. The thermogram shows a peculiar striped features (C) representing a macroscopic map of the subsurface damage distribution.

European dimension

This work represents a contribution to the network of activities in the field of the analysis of the conservation state of ancient books and of the deterioration of paper and parchment. In particular with this research we have developed an original application aimed at implementing non-invasive diagnostics, a fundamental task in this research field, to which recent coordinated activities such as the European thematic network on *metal in paper* (MIP) and the European joint research project on *methods of micro analysis of parchment* (MAP) can be referred to.

Innovation and originality

With this work we propose a new method for non-invasive depth profiling analysis of the samples (employable even in situ), of its assembly state, and of the adhesion of its different parts. Such an analysis can also be viewed as complementary to other used techniques (x-rays, tomographic, optical, etc.). Concerning parchment, with this research we have found some physical quantities (related to thermal transport) whose value depends on the deterioration state of the material.

Impacts

By the methodology that this work proposes, the structure of the historical bindings can be analysed without dismantling them providing an important evaluation tool in any restoring and/or conservation plan. One of the results of the present research is that the deterioration processes make the parchment properties progressively more isotropic. This aspect has been pointed out by mean of thermal diffusivity measurements and this suggests that such measurements can lead to a new non-invasive tool (non-destructive and non-contact) to quantitatively evaluate particular types of microstructural deterioration of parchment.

Acknowledgment

The authors wish to thank Jana Kolar, Matija Strlič and Gianluca Verona Rinati for their support in the samples preparation and SEM analysis.

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EVALUATING THE CONDITION OF PAPER

Jana Kolar[1], Matija Strlič[2], Tomasz Lojewski[3], Aneta Balažic[1], Drago Kočar[2], Špela Habicht[1]

1. National and University Library, Slovenia,
2. University of Ljubljana, Faculty of Chemistry and Chemical Technology, Slovenia, **3.** Jagiellonian University, Poland

PAPERTREAT

SurveNIR

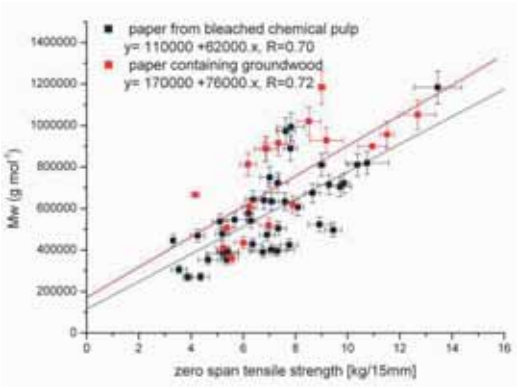

Fig. 2: Correlation between zero span strength and Mw of carbanilated cellulose for 62 historical papers made from bleached chemical pulp (black) and 17 historical papers containing groundwood (red). Error bars represent standard deviation.

Acknowledgments
The authors gratefully acknowledge the support of the European Community, 6th Framework Programe, contract no. SSPI-006584 (PaperTreat) and SSPI-006594 (*Surve*NIR). The work is the sole responsibility of the authors and does not represent the opinion of the Community.

During degradation, paper becomes increasingly more brittle, until it may no longer be handled safely. The condition of paper may therefore be determined by one of many different standard methods, which cover determination of various mechanical properties. However, due to numerous factors, such as the inhomogeneity of paper, repeatability is low and numerous measurements are needed to obtain a reasonably reliable result. Consequently, a large surface area, often a page or two is needed per experiment, which presents a serious drawback when evaluating the condition of a historical paper.

It had been demonstrated that a decrease of fibre strength is largely due to the depolymerisation of its main structural component, cellulose. Average molar mass of macromolecules is usually determined using a technique called size exclusion chromatography (SEC). Recently it was demonstrated that only a few fibres are needed for the analysis, when cellulose is derivatised using phenyl isocyanate.[1] However, due to the problems with dissolution, the technique was so far limited to fibers, whose lignin content was below a few percent. Two recent contributions demonstrated that lignin containing paper may be characterized using SEC, when the samples were derivatised using ethyl isocyanate.[2],[3] However, the technique still requires an ample amount of sample. In the present study, determination of an average molar mass of cellulose from randomly selected historical paper samples (0.2 mg), carbanilated with phenyl isocyanate, was attempted and the results were compared to zero span strength of paper (Fig 2).

A correlation between the average molar mass and zero span strength is observed for papers made from bleached chemical pulp as well as the ones that contained groundwood. The pronounced data scatter confirms that molar mass of cellulose in papers is not the only parameter in the correlation; however, it is evidently a significant one. The new methodology thus offers possibility to evaluate the condition of paper, even the one containing groundwood, from a few fibers only.

References

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2. Berthold, F., Gustaffson, K., Berggren, R., Sjöholm, E., & Linström, M. “Dissolution of Softwood Kraft Pulps by Direct Derivatisation in Lithium Chloride/*N,N*-Dimetylacetamide”. *J. Appl. Polym. Sci.*, **94**, 2004, pp. 424-431.

3. Kočar, D., Strlič, M., & Kolar, J. Degradation of lignin-containing paper: a new analytical methodology. 2nd International iron gall ink meeting, 2006, 66-67.

Evaluating the condition of paper

Aneta Balažic[1], Jana Kolar[1], Matija Strlič[2], Tomasz Lojewski[3], Drago Kočar[2] and Špela Habicht[1]

[1] National and university library, Slovenia
[2] University of Ljubljana, Faculty of Chemistry and Chemical Technology, Slovenia
[3] Jagiellonian University, Poland

Key words: paper, condition, size exclusion chromatography, cellulose

Introduction

During degradation, paper becomes increasingly more brittle, until it may no longer be handled safely. The condition of paper may therefore be determined by one of many different standards methods, which cover determination of various mechanical properties. However, due to numerous factors, such as the inhomogeneity of paper, repeatability is low and numerous measurements are needed to obtain a reasonably reliable result. Consequently, a large surface area, often a page or two is needed per experiment, which presents a serious drawback when evaluating the condition of a historical paper.

Results

It had been demonstrated that a decrease of fibre strength is largely due to the depolymerisation of its main structural component, cellulose. Average molar mass of macromolecules is usually determined using size exclusion chromatography (SEC). Recently it was demonstrated that only a few fibres are needed for the analysis, when cellulose is derivatised using phenyl isocyanate [1].

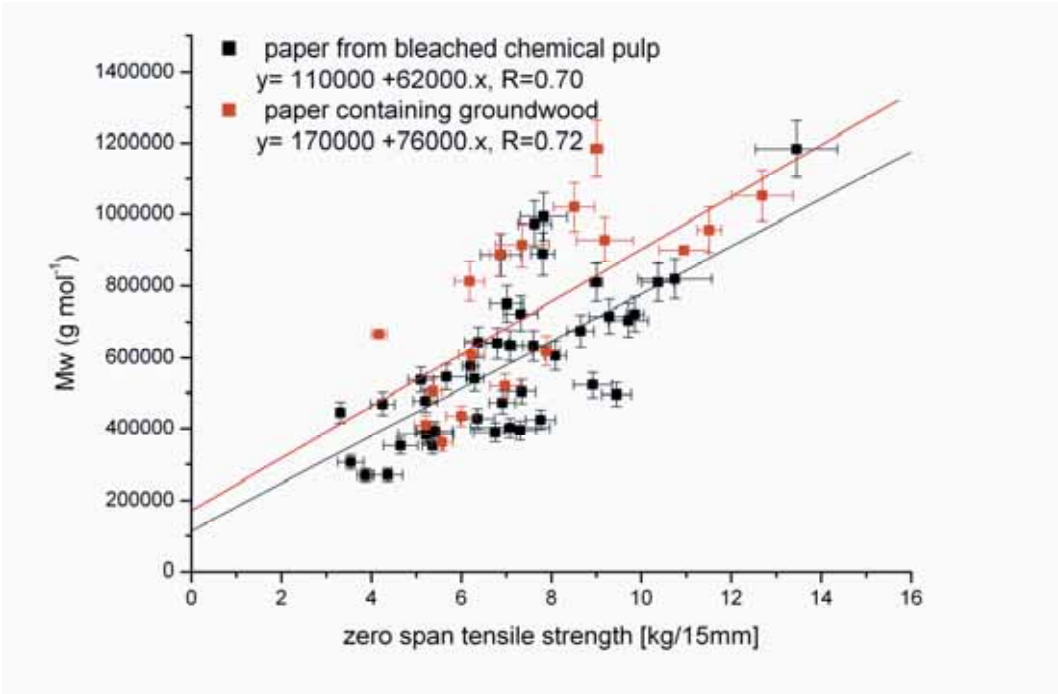

Figure 1: Correlation between zero span strength and Mw of carbanilated cellulose for 62 historical papers made from bleached chemical pulp (black) and 17 historical papers containing groundwood (red). Error bars represent standard deviation.

However, due to the problems with dissolution, the technique was so far limited to fibers, whose lignin content was below a few percent. Two recent contributions demonstrated that lignin containing paper may be characterized using SEC, when the samples were derivatised using ethyl isocyanate [2, 3]. However, the technique still requires an ample amount of sample. In the present study, cellulose from randomly selected historical paper samples (0.2 mg) was carbanilated with phenyl isocyanate, after which its average molar mass was determined. This was then compared to zero span strength of paper.

A correlation between the average molar mass and zero span strength is observed for papers made from bleached chemical pulp as well as the ones that contained groundwood. The pronounced data scatter confirms that molar mass of cellulose in papers is not the only parameter in the correlation; however, it is evidently a significant one. The new methodology thus offers possibility to evaluate the condition of paper, even the one containing groundwood, from a few fibers only.

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References
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EFFECT OF STABILIZATION PROCEDURES ON WOOD CONTAINING PAPER

Alena Maková[1], Bohuslava Havlínová[2], Linda Cszefalvayová[2]

[1]*Slovak National Library, J.C. Hronského 1, 036 01 Vrútky, Slovak Republic*
Faculty of Chemical and Food technology STU, Department of Polymeric Materials, Radlinského 9, Bratislava, Slovak Republic

Introduction

Hydrolytic and oxidative reactions strongly influence physical-mechanical as well as chemical properties of paper material and in turn cause a loss of its macroscopic properties. This is manifested in lower mechanical stability that may lead to full disintegration of paper sheets.

In paper conservation and restoration, much interest has focused on mass treatment of papers in an effort to solve the problem of strengthening of the weakened paper and improving the properties combined with the chemical stabilization of paper.

European dimension

Results of the experiments are used to throw more light upon the effect of various stabilization procedures on wood containing paper. This is a challenge, particularly important in the case of wood containing paper, since there are numerous collections of paper artefacts confronted with extensive damage caused by progressive natural ageing of paper following the degradation processes in paper. Considering the tested paper properties, application of antioxidant achieved appreciable good results with markedly stabilizing effect on paper. That is, advances obtained here in this study suggested the potential employment of such combination in stabilization of wood containing papers. Application of antioxidant provided the best stability on ageing together with slowing down the ageing processes in paper, compared to the other tested procedures.

Innovation

In paper conservation and restoration, much interest has focused on mass treatment of papers in an effort to solve the problem of strengthening of the weakened paper and improving the properties combined with the chemical stabilization of paper. Selected stabilization procedures in the present study, with the emphasis placed on application of antioxidant and mechanical

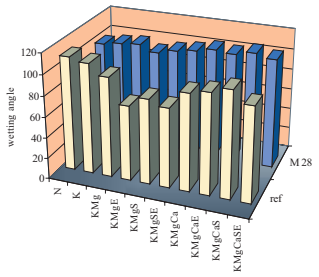

Fig.1 Effect of treatments on wetting angle for unaged samples and samples aged for 28 days at 80°C and 65% RH.

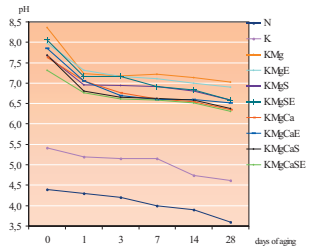

Fig.2 Change of pH for unaged samples and samples aged for 28 days at 80°C and 65% RH

This work was supported by Science and Technology Assistance Agency (Slovakia) under the contract No. APVT-20-30 4202 Ministry of education of the Slovak Republic for the financial support of project KNIHA.SK.

Experiment

Immersion of the groundwood acidic paper (80 g/m^2, pH = 4,4) sheets in ***deionized water*** (abbreviation **K**) for 15 min was carried out in order to wash out the soluble acid-paper degradation products

Combination of magnesium and calcium ions, in the form of their aqueous solutions, were chosen to neutralize the paper as well as to introduce sufficient alkaline reserve to the paper. The following solutions were used: *aqueous* ***magnesium bicarbonate solution Mg(HCO$_3$)$_2$*** in a concentration c = 0,1 mol/dm^3 (abbreviation **Mg**) followed by *aqueous* ***calcium bicarbonate solution Ca(HCO$_3$)$_2$*** in a concentration c = 0,01 mol/dm3 (abbreviation **Ca**). These deacidification treatments (applications of single neutralization solutions) are compared with other stabilizing procedures.

Aqueous solution of ***potassium iodide KI*** (abbreviation **S**) in a concentration c = 0,01 mol/dm^3 was used as a preventive treatment in order to decrease photo-induced degradation of paper.

Strengthening of paper by sizing with cationic starch derivate for the purpose of the mechanical stabilization of paper was

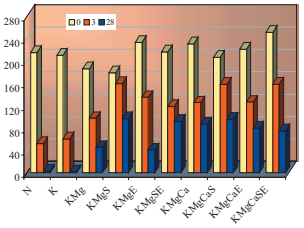

Fig.3 Change of folding endurance for paper samples treated in particular ways and aged at 80°C and

Conclusion

● *Neutralization* using magnezium bicarbonate (Mg) provided an increased **hydrophility** of paper surface together with the velocity of rinsing that increased significantly. This tendency is even more stressed after application of calcium bicarbonate (Ca) on papers previously neutralized with magnezium bicarbonate.

Combination of Mg together with Empresol (E) was responsible for increased wettability of paper. On the contrary, combination KMgCaE resulted in only slight decrease of wetting power of paper, due to the application of neutralization agents, as well as significant raise in time needed for sinking in paper surface.

Antioxidant (S) applied after neutralization with Mg made paper surface more hydrophilic (but to a less extent than E). The opposite tendency was observed when applied S after KMgCa (significant drop in surface hydrophility for samples KMgCaS).

Combination SE used after neutralization with Mg caused further decrease in hydrophility of paper surface (but incresed the time for sinking in paper surface) But the same combination applied after neutralization KMgCa resulted in a significant increase in surface hydrofility. The applications of E and S themselves appeared to lead to an incresed water resistance of paper, however, on the other hand, there was a pronounced increase of time for sinking in paper surface.

● Each stabilization treatment caused an increase of **pH** of origin paper in the following order K, KMgCaSE, KMgCa , KMgS, KMgCaS, KMgCaE, KMgE, KMgSE, KMg. As seen (Fig.2), *washing itself with deionized* water (K) slightly shifted pH of papers to higher values, since soluble acidic degradation products present in paper were partly washed out.

Of the tested stabilization procedures, *neutralization using magnezium bicarbonate* was found to increse pH values the most (as much as 54,2%). Application of each subsequent treatment led to the decrease of pH of paper already treated. The exception is application of E and S after KMgCa that caused the increase of pH of paper, however, using E and S just after KMg decrease the pH value.*Netralization with calcium bicarbonate* (KMgCa) shifted pH to lower values (about 8,7% decrease with regard to KMg).

The highest values of alkaline reserve were achieved if the paper was deacidified with a single magnesium bicarbonate solution (KMg), and each subsequent treatment was ineffective and caused a decrease of alkaline reserve.

Application of antioxidant improved the paper .properties under study and provided the best stability on ageing together with slowing down the ageing processes in paper, compared to the other tested procedures.

● *Application of antioxidant S* appears to be the most effective in inhibiting the mechanical deterioration of the aged samples, thus increasing the mechanical stability of the papers (43,9% decrease in **folding endurance** after 28 days of accelerated ageing for KMgS samples and 42,9% decrease for KMgCaS samples). Distinctive decrease of the folding endurance of the samples subjected to additional sizing with Empresol N occured (43,51% for samples KMgSE and 63,5% for samples KMgCaSE). At this point, it has to be noted that folding endurance decreases faster for the combination of both steps antioxidant-Empresol N than for treatment with antioxidant only.

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It is worth mentioning the difference between decrease in folding endurance for samples treated with magnezium bicarbonate (KMg) with the pronounced 69,3% reduction, while such decrease for KMgCa samples was 34,5%.

Effect of stabilization procedures on wood containing paper

Alena Maková[1], Bohuslava Havlínová[2] and Linda Csefalvayová[3]

[1] Slovak National Library, J.C. Hronského 1, SK-036 01 Vrútky, Slovak Republic
[2] Department of Polymeric Materials, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37, Bratislava, Slovak Republic
[3] Department of Physical Chemistry and Chemical Physics, Slovak University of Technology in Bratislava, Slovak Republic

Key words: deacidification, stabilization, sizing, cationic starch derivate, antioxidant

Introduction and content

Hydrolytic and oxidative reactions strongly influence physical-mechanical as well as chemical properties of paper material and in turn cause a loss of its macroscopic properties. This is manifested in lower mechanical stability that may lead to full disintegration of paper sheets.

The aim of the present work is to evaluate and make a proper selection of the stabilization process considering the following steps: removal of acid soluble products from wood containing paper; inhibiting the oxidative degradation of paper by application of antioxidant potassium iodide KI; neutralization of free acid present in paper coupled with the inclusion of alkaline reserve to protect paper against ageing and new acidity by application of magnesium bicarbonate $Mg(HCO_3)_2$ and calcium bicarbonate $Ca(HCO_3)_2$; mechanical strengthening of paper by sizing it with cationic starch derivate Empresol N.

European dimension

Results of the experiments are used to throw more light upon the effect of various stabilization procedures on wood containing paper. This is a challenge, particularly important in the case of wood containing paper, since there are numerous collections of paper artefacts confronted with extensive damage caused by progressive natural ageing of paper following the degradation processes in paper. Considering the tested paper properties, application of antioxidant achieved appreciable good results with markedly stabilizing effect on paper. That is, advances obtained here in this study suggested the potential employment of such combination in stabilization of wood containing papers. Application of antioxidant provided the best stability on ageing together with slowing down the ageing processes in paper, compared to the other tested procedures.

Innovation and originality

In paper conservation and restoration, much interest has focused on mass treatment of papers in an effort to solve the problem of strengthening of the weakened paper and improving the properties combined with the chemical stabilization of paper. Selected stabilization procedures in the present study, with the emphasis placed on application of antioxidant and mechanical strengthening of paper, are addressed to single sheet treatment where aqueous treatments can be applied.

Impacts

The paper substrate used in *experimental part* was groundwood acidic paper (80 g/m^2, pH = 4,4) made in Slavošovské papierne, Slavošovce, Slovak Republic. In this contribution, a comparison of several treatments is presented. Tested papers were treated with deionized water, magnesium bicarbonate, calcium bicarbonate, potassium iodide and Empresol N. The samples were artificially aged under ISO STN 563 conditions (moist heat ageing): 80 °C, 65% RH for up to 28 days, respectively 0, 1, 3, 7, 14 and 28 days.

Immersion of the paper sheets in *deionized water* (abbreviation *K*) for 15 min was carried out in order to wash out the soluble acid-paper degradation products. Combination of magnesium and calcium ions, in the form of their aqueous solutions, were chosen to neutralize (deacidify) the paper as well as to introduce sufficient alkaline reserve to the paper. The following solutions were used: *aqueous magnesium bicarbonate solution* $Mg(HCO_3)_2$, in a concentration c = 0,1 mol/dm^3 (abbreviation *Mg*) followed by *aqueous calcium bicarbonate solution* $Ca(HCO_3)_2$ in a concentration c = 0,01 mol/dm^3 (abbreviation *Ca*). These deacidification treatments (applications of single neutralization solutions) are compared with other stabilizing procedures. *Aqueous solution of potassium iodide KI* (abbreviation *S*) in a concentration c = 0,01 mol/dm^3 was used as a preventive treatment in order to decrease photo-induced degradation of paper. Strengthening of paper by sizing with cationic starch derivate for the purpose of the mechanical stabilization of paper was carried out with the aqueous solution of *Empresol N* in a 1,5 % (w/w) concentration (abbreviation *E*).

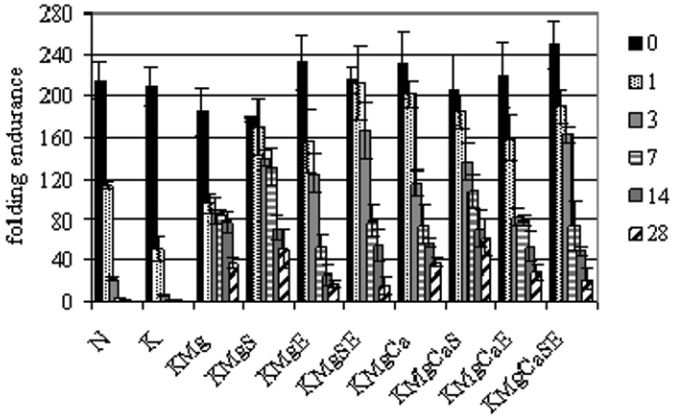

Figure 1: Change of folding endurance for paper samples treated in particular ways and aged at 80 °C and 65% RH

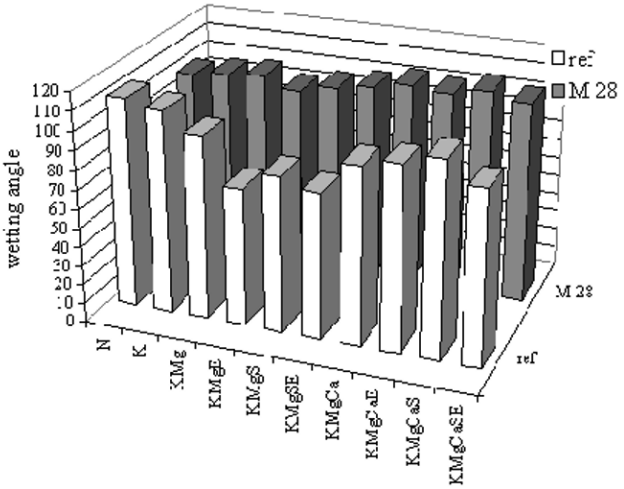

Figure 2: Effect of treatments on wetting angle for unaged samples and samples aged for 28 days at 80 °C a 65% RH

Each stabilization treatment caused an increase of pH (Fig. 1) of origin paper in the following order K < KMgCaSE < KMgCa < < KMgS < KMgCaS < KMgCaE < KMgE < KMgSE < KMg. Of the tested stabilization procedures, neutralization using magnezium bicarbonate was found to increase pH values the most (as much as 54,2%). Application of each subsequent treatment led to the decrease of pH of paper already treated. The exception was application of E and S after

KMgCa that caused the increase of pH of paper, however, using E and S just after KMg decreased the pH value. Netralization with calcium bicarbonate (KMgCa) shifted pH to lower values (about 8,7% decrease with regard to KMg). The highest values of alkaline reserve were achieved if the paper was deacidified with a single magnesium bicarbonate solution (KMg), and each subsequent treatment was ineffective and caused a decrease of alkaline reserve. The values of alkaline reserve of papers were higher when using magnezium bicarbonate (Mg) than that of papers treated with the combination of both neutralization solutions (MgCa).

After moist heat ageing, there was a drop in the values of alkaline reserve for papers that have been subjected to a treatment with antioxidant, KMgCaS and KMgSE, and application of Empresolu N resulted in further decrease of alkaline reserve. The lowest decrease of alkaline reserve, concerning the origin paper, were obtained for samples treated with the combination KMgSE (26,3%), MgE (28%) and KMgCaS (31,25%). The most pronounced drop in the values of alkaline reserve showed the following combination of treatments KMgCa (50% reduction) and KMgCaSE (41,3% reduction).

Application of antioxidant S appeared to be the most effective in inhibiting the mechanical deterioration of the aged samples, thus increasing the mechanical stability of the papers (43,9% decrease in folding endurance after 28 days of accelerated ageing for KMgS samples and 42,9% decrease for KMgCaS samples).

Neutralization using magnesium bicarbonate (Mg) provided an increased hydrophility of paper surface together with the velocity of rinsing that increased significantly. This tendency was even more stressed after application of calcium bicarbonate (Ca) on papers previously neutralized with magnesium bicarbonate. Combination of Mg together with Empresol N (E) was responsible for increased wettability of paper. On the contrary, combination KMgCaE resulted in only slight decrease of wetting power of paper, due to the application of neutralization agents, as well as significant raise in time needed for sinking in paper surface. Antioxidant (S) applied after neutralization with Mg made paper surface more hydrophilic (but to a lesser extent than E). The opposite tendency was observed when applied S after KMgCa (there was a significant drop in surface hydrophility for samples KMgCaS). Combination SE used after neutralization with Mg caused further decrease in hydrophility of paper surface (but increased the time for sinking in paper surface) But the same combination applied after neutralization KMgCa resulted in a significant increase in surface hydrophility. The applications of E and S themselves appeared to lead to an increased water resistance of paper, however, on the other hand, there was a pronounced increase of time for sinking in paper surface (Fig. 2).

Acknowledgement

Ministry of education of the Slovak republic is gratefully acknowledged for the financial support of projects KNIHA.SK. We thankfully acknowledge the support provided by Science and Technology Assistance Agency (Slovakia) under the contract No. APVT-20-30 4202.

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Transition Metals in Paper
EU Thematic Network
EVK4–CT-2002-20010

Thematic Framework

Fifth Framework Programme of the
European Commission, DG Research.
Energy, Environment and Sustainable Development.
City of Tomorrow and Cultural Heritage

Aims and Goals

- Exchange knowledge
- Establish needs for new innovative conservation strategies
- Strategy: assessment methods and treatment technologies
- Interface between science and end-users

Basics

- Focus: (ligno-) cellulosic materials
- 21 official partners from all over Europe
- Combining 3 disciplines:
  - (Paper) Conservation science:
    Research institutes, universities
  - Suppliers in (paper) conservation technology
    SME-s, Technology suppliers
  - End users
    Restoration workshops, Policy makers and collection keepers (museums, archives, libraries)

European Dimension/Partners

TNO – The Netherlands Organization for Applied Scientific Research
National Archives of Sweden
National Archives of The Netherlands
Zentrum für Bucherhaltung GmbH, Germany
Museu Molí Paperer de Capellades, Spain
Slovak Technical University, Slovakia
University of Northumbria, United Kingdom
Göteborg University, Sweden
Slovak National Archives, Slovakia
National Archives of Estonia
National and University Library, Slovenia
National Library of Norway
Art Innovation, The Netherlands
Institute of Cultural Heritage, The Netherlands
University of Ljubljana, Slovenia
CNR-ISMN, Italy
Quillet S.A., France
University La Rochelle, France
Museum Boijmans Van Beuningen, The Netherlands
IVTEK, Finland
Jagiellonian University, Poland

Technology themes

Four theme groups

1. Fundamental Studies
   Chair Matija Strlic, Slovenia
2. Active Conservation – Chemical Aspects
   Chair Jana Kolar , Slovenia
3. Active Conservation – Physical Aspects
   Chair Manfred Anders , Germany
4. Preventive conservation
   Chair John Havermans, Netherlands

Web-site

Project Funding

European Commission, DG Research

All participating members

Coordinator & Contact

TNO Building and Construction Research
Dr J.B.G.A. Havermans
Phone: +3115 276 33 13
PO BOX 6031 Fax : +3115 276 30 23
2600 AA Delft
The Netherlands
E-mail: j.havermans@bouw.tno.nl

MIP – three years networking

J.B.G.A. Havermans

TNO Built Environment and Geosciences, Po Box 49, 2600 JA Delft, The Netherlands
E-mail: john.havermans@tno.nl

Introduction

The role of a network is to improve contacts between researchers and key persons in a similar field. For MIP (Transition Metals In Paper) it was the field of paper degradation and the role of the (transition) metals in the paper substrate. Degradation of the paper substrate is not our main goal actually but preventing it for further degradation and to find solutions in conservation. Therefore dissemination of work in this field from MIP to MIP members and from MIP to non-MIP members and vice versa was an important action in the organization during the MIP-age. As we were dealing with four working groups, the main reached goals will be summarized

European dimension

36 months, 21 official participants, 10 official technical meetings, and many more individual meetings, four theme groups and a lot of talks were forming the heart of the EC thematic network MIP EVK4-CT-2002-20010. Results of the network can be seen as significant for the European field of conservation and conservation research. New co-operations were established between MIP countries and non-MIP countries; new research proposals were initiated within the 6th Framework program of the EU and new networking proposals for example under the COST umbrella was initiated. Reaching initially the 9 participating MIP countries, in January 2006 we reached in total 20 participating countries including Australia, Canada and the USA.

Innovation and originality

The aim of the network is to respond collectively to specific threats to European paper based cultural heritage in relation to transition metals in paper. Components that are present in the paper substrate due to the applied ink (metal tannin ink), impurities in the water (iron traces) or deacidification. Four theme groups (TG) have been established to discuss and cluster their specific topics. The groups are based on both fundamental issues and applied issues such as applications. TG-1 covered the fundamental scientific aspects of paper degradation focusing primarily on diagnostic and analytical techniques, studies of degradation processes (including endogenous and exogenous factors), and methodologies for paper stability evaluation. TG-2 covered the chemical aspects of active conservation while TG-3 worked on the physical aspects of active conservation. Finally TG-4 was dealing with preventive conservation issues.

Impact

Theme group 1: fundamental research / analyses

Fundamental research of paper and cellulose degradation was in the focus of three large-scale research programs in Europe.

1. The EC InkCor project.
   The degradation of paper caused by iron gall ink was investigated extensively in order to find preservation solutions. Interfering with the autoxidation processes proved to be the conservation strategy of choice.
2. The EU Papylum project.
   A novel instrument for investigating oxidation of paper / cellulose was developed and the kinetics of autoxidation was investigated. Based on the acquired knowledge, and on extensive studies of real papers, water-based deacidification processes were optimised.

3. The Polish research programme on mass deacidification and preservation. Studies were done on the effect of alum on paper degradation, and on the application of deacidification.

Besides these large projects, research on the degradation of paper / cellulose in order to understand the need for prevention and storing the materials under the correct circumstances took place in many national projects Considerable work still has to be done to understand the aging of paper in real conditions. While it was demonstrated that a wide variety of *analytical methods* are used and provide extremely relevant information, it was also evident that there is a pronounced need for non- and micro-destructive analytical tools. On the scientific side such tools would be needed to study the conditions of real objects, the effects of the environment on an object, to identify ink components etc. On the side of a conservator, there is a real need for simple identification, diagnosis and monitoring tools, e.g. for identification of inks, material composition or quality. Based on a MIP meeting dedicated to spectroscopy, some interesting applications are already available. However, many of these require operation by a conservation scientist and a proper interpretation is still needed for conservation/preservation workers. New networks and improved education could assist to bring both together.

Theme group 2: Active conservation – chemical aspects
Chemicals are frequently used at conservation workshops. From cleaning to deacidication, from bleaching to sizing. Current groups of chemicals in use are for example: alkalies, buffers, oxidising and reducing agents used for bleaching of paper, chelators for the removal of rust, organic solvents for the removal of pressure sensitive tapes. However, the impact of many of the chemicals on the stability of the objects seems to be insufficiently researched and often based on the experience of the user. Additional problems are related to safe handling and disposal of chemicals. It was therefore concluded that educational programs are needed to ensure the safe usage, handling and disposal of chemicals in conservation. It also became evident that the communication between scientists, which develop the conservation treatments and conservators, which use them, needs to improve significantly. Increased cooperation of specialists from different disciplines is considered one of the major achievements of the MIP project, which will enable the development of best practices in conservation research as well in conservation.

Theme group 3: Active conservation – physical aspects
For a complete treatment of papers that are damaged by ink corrosion, it is necessary to know the fundamental scientific aspects of this degradation mechanism and the chemical aspects of active conservation by special treatments. In the EU project “InkCor” methods for the deacidification and the anti-oxidative treatment were developed and tested. The results were presented on several MIP-symposiums. These treatment methods are really effective for the treatment of slight ink corrosion. In the cases of advanced ink corrosion where, besides deacidification and anti-oxidative treatment, also a new consolidation and a void completion is necessary, the new results have to be adapted with the known conservation methods of paper consolidation (leaf casting, lining / backing, paper splitting). The evaluation of the most suitable materials (fibres, glue, stabilizing matrix), deacidification agents and antioxidants is also necessary. For the survey of the real “state of art” in the conservation workshops, the questions and requirements in the treatment of ink corrosion, a questionnaire was prepared, which is spread internationally and shall detect the requirements of conservators for future activities. MIP members will continue to apply their connections as started by MIP and will search for new opportunities to continue their cooperation and find ways to improve active conservation aspects.

Theme group 4 – Preventive conservation
Based on the gained knowledge by the MIP meetings, conclusions can be drawn on the serious role of the *environment* during storage and exhibition of objects affected with iron gall ink

corrosion. However good-storage conditions are not defined on EU-level. Fortunately storage conditions for objects in archives, libraries and museum are presented in ISO standards and in some cases given by Law. For example the Netherlands is so far know, the first country that established the storage conclusions in the Archival Act law. However questions do arise if these conditions are indeed suitable for the storage of MIP objects. Based on studies by the InkCor and PaPyLum projects as well as studies from national project (e.g. the ink corrosion project in the Netherlands, 2000), it can be shown easily that good storage conditions for MIP objects differ from normal objects. This is due to the reactions taken place in the objects (oxidation, hydrolyses and cross linking ones). Also the exhibition of the objects has to be done with care. ISO standards for exhibition should be applied, or even better more serious standards have to be developed. Light here is one of the main factors as light my not only cause a direct visual colour change; it also can promote the deterioration due to the radiation in the light. Based on the discussions in MIP, conclusions can be drawn to establish new standards for storage and exhibition environment of MIP objects.

One of the issues found, is that objects affected with IGI can emit organic components. The emission is due to the 'natural' ageing of the substrate and the ink. Components as acetic acid and furfural were found. The components can react with the objects causing a kind of auto-degradation. Therefore recommendations can be given on the need of storage in well-ventilated areas preferable with air purification. It also is recommended to obtain more studies to the possibility of auto-degradation. Frequently the topic of *damage identification* was mentioned during discussions related to preventive conservation. Although this subject falls under analyses, some words will be written here to identification. Especially when objects are given to exhibition one is not aware what the effects of that exhibition would be in terms of chemical and physical change of the object. The need for non-destructive tools to verify the state and quality of the object are therefore necessary.

Conclusions

MIP resulted in 3 international projects. Two research projects funded within the 6th Framework program of the European Commission: the PaperTreat project and the Survenir Project (both started end 2005) and the EU COST D42 Action on interactions between artifacts and the indoor environment. MIP members are play a key role in these projects.

Due to the MIP Network, knowledge on the degradation of paper especially in relation with metal (ions) increased. The EU cooperation and dissemination resulted in an improvement of knowledge applicable for both fields: research and application. However there is a lack of education and education materials. The need for textbooks in conservation and science is needed. Although new initiatives on research were successful, we must conclude that more research and applied research is needed to preserve our heritage for the future. To identify the needed topics. Networking can be seen as a perfect tool. The need at both local and EU level for financial support of conservation and research actions remains needed and should be improved in the 7th EU framework program. Also it has to be concluded that education programmes should be developed that fit the needs of conservators / preservation workers.

Acknowledgement

We would like to express our thanks to the European Commission DG Research to have this network funded under their framework program contract EVK4-CT-2002-20010.

European project details

MIP Contract no. EVK4-CT-2002-20010. Transition Metals In Paper. Coordinator Dr. John Havermans, TNO, Delft, The Netherlands.

APPLICATION OF EPR SPIN TRAPPING TECHNIQUE IN THE INVESTIGATION OF RADICAL INTERMEDIATES INVOLVED IN PAPER DEGRADATION

Linda Csefalvayova*, Vlasta Brezova* and Bohuslava Havlinova**

* Department of Physical Chemistry and Chemical Physics, Slovak University of Technology in Bratislava, Radlinskeho 9, SK-812 37, Slovak Republic

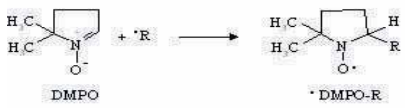
** Department of Polymeric Materials, Slovak University of Technology in Bratislava, Slovak Republic

Introduction

Our experiments are focused on the investigation of reactive radical species (hydroxyl radicals etc.) produced upon ageing of pure cellulose paper in the presence of transition metal ions by means of EPR (Electron Paramagnetic Resonance). In the present work, the in situ EPR experiments showed evidence of the free radical formation that have been recognized as being important causative agents of ageing of paper supports. Hydroxyl radicals and hydroperoxidic structures play the role of intermediates in the oxidation reactions of paper supports.

Innovation and Originality

It is generally admitted that metal-catalyzed oxidation mechanism of paper supports proceeds via free radical intermediates [1]. The identification of free radicals is crucial to assess the mechanisms of free radical chain pathways and the spin trapping technique is a convenient approach to understand the complex oxidation reactions in the area of cellulose degradation. The detection methods include the electron spin resonance-spin trapping method. ***EPR*** is a highly sensitive technique for detection (<10-8 M) and identification of molecules with an unpaired electron (paramagnetic species). ***EPR spin trapping method*** involves the inclusion in the experimental system of a diamagnetic EPR silent compound (spin trap) that can react with a short-lived free radical such as •OH via addition to a spin trap double bond, producing a more stable free radical product (spin adduct). Spin adducts are paramagnetic and are usually detected by EPR spectroscopy.



Hydroxyl radicals were detected by the electron spin resonance spectroscopy coupled to the spin trapping technique using the 5,5-dimethyl 1-pyrroline N-oxide (DMPO) as spin trap agent. The spin adduct DMPO/HO• resulting from the trapping of HO• with DMPO, showed a characteristic electron spin resonance signal.

Experimental Part

EPR measurements at the X-band were performed with a Bruker EMX EPR spectrometer equipped with a TM-110 (ER 4103 TM) cylindrical cavity. In EPR experiments Whatman No. 1 paper samples were immersed for approximately 10 seconds in a 5×10–3M aqueous solutions of FeSO4 and CuSO4, respectively and then dried in an ambient atmosphere. Paper samples were aged artificially in enclosed glass bottle sealing and heated to 100 °C for half an hour up to 8 hours. We deposited on paper 50 µl of 0.2 mol dm–3 DMPO.

Results

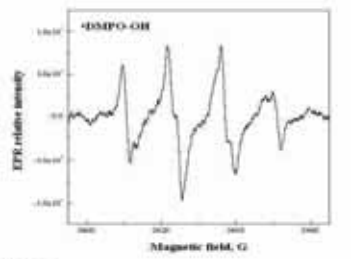


Figure 1.
Experimental EPR spectra with the signal attributed to DMPO spin adduct with hydroxyl radical.

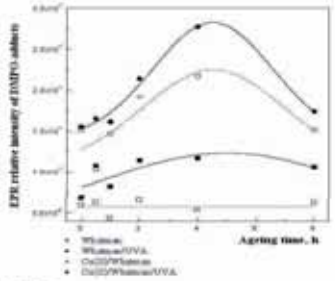


Figure 2.
The figure represents the dependence of the •DMPO-OH relative integral intensity of EPR signal on the ageing time of Whatman paper samples treated with the Cu(II) solution and consequently irradiated in situ (Cu(II)/Whatman/UVA) or without irradiation (Cu(II)/Whatman) and pure Whatman paper (Whatman and Whatman/UVA).

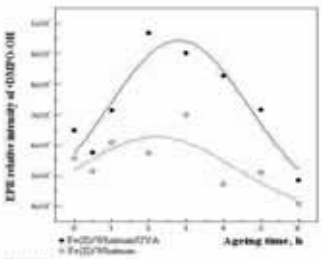


Figure 3.
The figure represents the dependence of the •DMPO-OH relative integral intensity of EPR signal on the ageing time of Whatman paper samples treated with the Fe(II) solution and consequently irradiated in situ (Fe(II)/Whatman/UVA) or without irradiation (Fe(II)/Whatman).

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We gratefully acknowledge the financial support provided by the Slovak Grant Agency (No. Project VEGA 1/3579/06).

Application of EPR spin trapping technique in the investigation of radical intermediates involved in paper degradation

Linda Csefalvayová[1], Vlasta Brezová[1] and Bohuslava Havlínová[2]

[1] Department of Physical Chemistry and Chemical Physics, Slovak University of Technology in Bratislava, Radlinskeho 9, SK-812 37, Bratislava, Slovak Republic
[2] Department of Polymeric Materials, Slovak University of Technology in Bratislava, Slovak Republic

Key words: electron paramagnetic resonance, spin trapping, radicals, paper degradation

Introduction and content

Our experiments are focused on the investigation of reactive radical species (hydroxyl radicals etc.) produced upon ageing of pure cellulose paper in the presence of transition metal ions by means of EPR (Electron Paramagnetic Resonance). In the present work, the in situ EPR experiments showed evidence of the free radical formation, in the few representative systems during accelerated ageing, that have been recognized as being important causative agents of ageing of paper supports. Hydroxyl radicals were detected by the electron spin resonance spectroscopy coupled to the spin trapping technique using the 5,5-dimethyl 1-pyrroline N-oxide (DMPO) as spin trap agent. The spin adduct DMPO/HO$^{\bullet}$ resulting from the trapping of HO$^{\bullet}$ with DMPO, showed a characteristic electron spin resonance signal. Hydroxyl radicals and hydroperoxidic structures (H_2O_2, ROOH etc.) play the role of intermediates in the oxidation reactions of paper supports. It is generally admitted that metal-catalyzed oxidation mechanism of paper supports proceeds via free radical intermediates [1].

European dimension

Identification of intermediates is essential to assess mechanisms, studied in the field of paper degradation research, that govern the reaction pathway. It is well established that hydroxyl radicals are the most important oxidizing species in the degradation reactions of paper supports. Nevertheless, concerning such processes, few studies are devoted to the identification of free radicals [2]. The detection of hydroxyl radicals in EPR experiments is not a routine technique and has also been a focus of some studies. Since the life time of a hydroxyl radical is ca. 10^{-9} s [3], it can only be detected indirectly. The detection methods include the electron spin resonance-spin trapping method.

EPR is a highly sensitive technique for detection ($<10^{-8}$ M) and identification of molecules with an unpaired electron (paramagnetic species). However, free radical intermediates are usually too short-lived to be directly detected by EPR spectroscopy. The spin trapping technique overcomes this problem: it consists of transforming short-lived reactive free radicals into more persistent paramagnetic species, by trapping free radicals on diamagnetic acceptor molecules (the spin traps are generally nitroso or nitrone compounds). The resulting product (spin adducts) that are nitroxide compounds and are sufficiently persistent to be readily observed by EPR spectroscopy at room temperature. Analysis of EPR spectra provides characteristic parameters (hyperfine splitting constants, g factor) which contain information on the initial trapped radicals. *DMPO* was used as spin trap in this study because of its excellent ability to trap O- and C-centered radicals.

Innovation and originality

Although free radicals are undoubtedly present in the degradation processes, to our knowledge, direct and positive evidences of identification of implicated radicals by EPR are scarce in literature and the formation of hydroxyl radicals in paper has not yet been established in such way using this appropriate instrumental method [4]. The identification of free radicals is crucial to assess the mechanisms of free radical chain pathways and the spin trapping technique is a convenient approach to understand the complex oxidation reactions in the area of cellulose degradation.

Impacts

EPR measurements at the X-band were performed with a Bruker EMX EPR spectrometer equipped with a TM-110 (ER 4103 TM) cylindrical cavity. The samples were irradiated at 293 K directly in the EPR spectrometer microwave cavity, and the EPR spectra were recorded in situ. As an irradiation source an HPA 400/30S lamp (400 W, Philips) was used; it is a medium-pressure metal halide lamp with iron and cobalt additives emitting ozone-free radiation mainly between 300 and 400 nm (λ_{max} = 365 nm). The source radiation was focused to obtain high intensity in the active part of the TM cylindrical resonator. In EPR experiments Whatman No. 1 paper samples (50 × 50 mm) were immersed for approximately 10 seconds in a 5×10^{-3}M aqueous solutions of $FeSO_4$ and $CuSO_4$, respectively and then dried in an ambient atmosphere. Paper samples were aged artificially by following method: samples were preconditioned at relative humidity 50 % (at 23 °C), afterwards enclosed into 300 ml glass bottle, covered by Viton (DuPontDow) sealing and heated to 100 °C for half an hour up to 8 hours. The photochemical experiments on the paper were performed on 200 mm^2 of Whatman paper. Firstly, we deposited on paper 50 µl of 0.2 mol dm^{-3} DMPO. Then, the solvent was evaporated under air, in the dark at room temperature. Then the sample was transferred to an EPR quartz tissue cell.

We presupposed the formation of paramagnetic radical species upon accelerated ageing of Whatman cellulose paper and autooxidation of cellulose during the storage procedure, generating hydroperoxides in accord with the generalized scheme [5] [Eqs. (1-3)]:

$$R{-}H \rightarrow R^{\bullet} + H^{\bullet} \quad (1)$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \quad (2)$$

$$ROO^{\bullet} + R{-}H \rightarrow ROOH + R^{\bullet} \quad (3)$$

Transition metal ions have the ability to undergo pseudo-Haber-Weiss cycle of hydroperoxides decomposition [1] [Eqs. (4, 5)]:

$$ROOH + Me^{n+} \rightarrow RO^{\bullet} + Me^{(n+1)+} + HO^{-} \quad (4)$$

$$Me^{(n+1)+} + ROOH \rightarrow ROO^{\bullet} + Me^{n+} + H^{+} \quad (5)$$

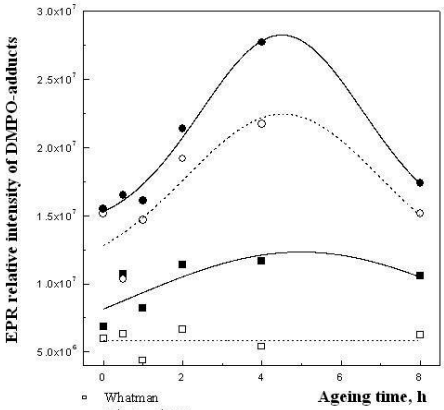
The decomposition of hydroperoxidic structures initiated by metal ions, heating or irradiation results in the formation of reactive oxygen radical intermediates [Eqs. (6, 7)], among which, the hydroxyl radical $^{\bullet}OH$ is presumed to play a central role due to its strong activity that may induce significant deterioration processes of paper substrates, leading to the loss of mechanical and optical properties.

$$ROOH + h\nu \rightarrow R^{\bullet} + {}^{\bullet}OOH \quad (6)$$

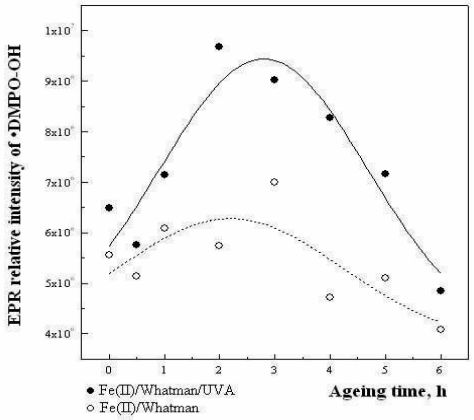
$$ROOH + h\nu \rightarrow RO^{\bullet} + {}^{\bullet}OH \quad (7)$$

This mechanism could rationally explain the formation of oxygen-centered radical adducts monitored upon irradiation of Whatman paper samples initially immersed in iron and copper ions solutions in the presence of spin trap DMPO, as is be demonstrated below on Figures 1-2.
It should be noted here that in all systems containing copper ions on Whatman substrate already prior to irradiation of samples, a paramagnetic signal attributed to $^{\bullet}$DMPO-OH was identified

and at higher level of signal intensity as in the case of iron – containing papers. The relative intensity of EPR signal reflecting •DMPO-OH formation upon ageing of pure Whatman paper samples is significantly lower comparing to metal ions containing papers. However, the signal is low but evident. The data obtained clearly demonstrated the importance of hydroperoxidic structures generated in paper by autooxidation or photochemical processes in the presence of metal ions.



1)



2)

Figure 1, 2: 1)The figure represents the dependence of the •DMPO-OH relative integral intensity of EPR signal on the ageing time of Whatman paper samples treated with the Cu(II) solution and consequently irradiated in situ (Cu(II)/Whatman/UVA) or without irradiation (Cu(II)/Whatman) and pure Whatman paper (Whatman and Whatman/UVA)
2) The figure represents the dependence of the •DMPO-OH relative integral intensity of EPR signal on the ageing time of Whatman paper samples treated with the Fe(II) solution and consequently irradiated in situ (Fe(II)/Whatman/UVA) or without irradiation (Fe(II)/Whatman)

Acknowledgement

We gratefully acknowledge the financial support provided by the Slovak Grant Agency (No. Project VEGA 1/3579/06).

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XANES AND MOESSBAUER ANALYSIS OF FE VALENCE IN IRON GALL INKS ON PAPER

Iztok Arčon[1,2], Jana Kolar[3], Darko Hanžel[2], Matija Strlič[3], Alojz Kodre[4,2]

1. University of Nova Gorica, Slovenia, **2.** Jožef Stefan Institute, Slovenia,
3. University of Ljubljana, Faculty of Chemistry and Chemical Technology, Slovenia, **4.** University of Ljubljana, Faculty of Mathematics and Physics, Slovenia

Rembrandt, detail, iron gall ink on paper, collection Teylers museum, The Netherlands.

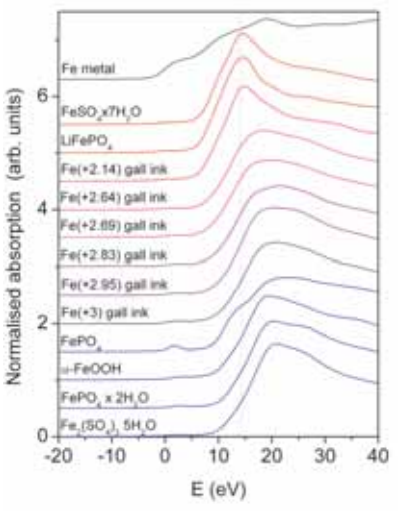

Fig. 2. Fe K-edge XANES spectra model iron gall inks on paper with average Fe valence state between Fe^{2+} and Fe^{3+} and standard Fe^{2+} (red) and Fe^{3+} (blue) reference compounds. Number in brackets denotes an average iron oxidation state in a sample.

Acknowledgments
This work was supported by the Slovenian Research Agency research programmes P1-0112 and P1-0153, by DESY and the European Community under the FP6 Programme »Structuring the European Research Area« contract RII3-CT-2004-506008 (IA-SFS). Access to synchrotron radiation facilities of HASYLAB (project II-04-065) and expert advice on beamline operation by Edmund Welter of HASYLAB is acknowledged.

Iron gall ink is one of the most important inks in the history of western civilization, of a widespread use from the middle ages until the 20th century. Unfortunately, the ink induces degradation of paper, causing severe damage to numerous historical artefacts. As a result, 60-70% of Leonardo da Vinci's oeuvre shows signs of deterioration, Bach's written music is virtually falling apart, while numerous manuscripts by Galileo Galilei are completely destroyed. The two main reasons for the decay are acid hydrolysis and oxidation, catalysed by ferrous ions. Determination of the ratio of Fe^{2+}/Fe^{3+} in the inks is therefore important for the understanding of the degradation process and in devising effective stabilization treatments.

In the present study, reliability of Fe K-edge XANES spectroscopy as a tool in determination of Fe^{2+}/Fe^{3+} ratio in historic inks was investigated.

Fe K-edge XANES spectra (Fig. 2) of different standard Fe(II) and Fe(III) iron reference compounds, and of several model iron gall inks with different Fe(II)/ Fe(III) ratio were acquired. The ratio in the latter was also determined using Moessbauer spectroscopy. X-ray absorption spectra were collected in transmission mode at E4 beamline of HASYLAB synchrotron facility at DESY in Hamburg. A Si(111) double crystal monochromator was used with about 1.5 eV resolution at the Fe K-edge (7112 eV). Equidistant energy steps of 0.3 eV were used in the Fe K-edge scans. Three repetitions were taken to assure the reproducibility. Exact energy calibration was established with simultaneous absorption measurements on a 5 mm thick Fe metal foil placed between the second and the third ionisation chamber. Absolute energy reproducibility of the measured spectra was 0.1 eV or better.

The results show that a proper choice of the Fe reference compounds with the same type of atoms in the first coordination shell of Fe ion and a similar local structure is crucial for the absolute calibration of the Fe K-edge shift and therewith reliable determination of Fe(II)/ Fe(III) ratio in the sample. In the specific case of iron gall inks, best results are obtained with $FeSO_4 \times 7H_2O$ as a reference for Fe(II) and a model iron(III) gall ink as a reference for Fe(III) XANES spectrum. Using a linear combination fit with these two spectra, it is possible to determine the amount of Fe(II) in the iron gall ink with the accuracy better than 5%.

XANES and Moessbauer analysis of Fe valence in iron gall inks on paper

Iztok Arčon[1,2], Jana Kolar[3], Darko Hanžel[2], Matija Strlič[3] and Alojz Kodre[4,2]

[1] University of Nova Gorica, Slovenia
[2] Jožef Stefan Institute, Slovenia
[3] University of Ljubljana, Faculty of Chemistry and Chemical Technology, Slovenia
[4] University of Ljubljana, Faculty of Mathematics and Physics, Slovenia

Key words: iron gall ink, XANES, Moessbauer, iron

Introduction

The corrosive properties of iron gall ink induce severe degradation of paper. The two main reasons for the decay are acid hydrolysis and oxidation, catalysed by ferrous ions [1]. Determination of the ratio of Fe^{2+}/Fe^{3+} in the inks is therefore important for the understanding of the degradation process and in devising effective stabilization treatments.

Results

In this study, the feasibility and reliability of Fe K-edge XANES spectroscopy as a tool in determination of Fe^{2+}/ Fe^{3+} ratio in historic inks was investigated. In XANES, the valence state of metal cations can be deduced from the shift of the absorption edge or pre-edge absorption features [2].

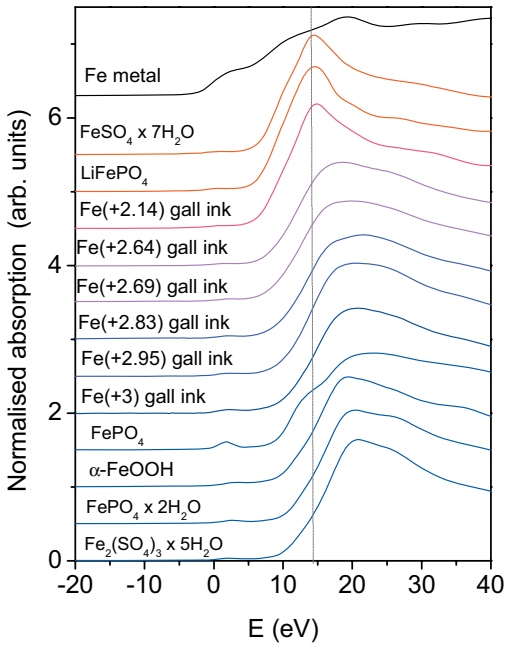

Figure 1: Fe K-edge XANES spectra model iron gall inks on paper with average Fe valence state between Fe^{2+} and Fe^{3+} and standard Fe^{2+} (red) and Fe^{3+} (blue) reference compounds. Number in brackets denotes an average iron oxidation state in a sample. The energy scale is relative to the Fe K-edge in Fe metal (7112 eV). The spectra are displaced vertically for clarity. The vertical dashed line is plotted at the position of the Fe K-edge in iron(III) gall ink to facilitate the comparison of edge shifts

For metal cations with the same type of atoms in the first coordination shell, a linear relation between the edge shift and the valence state was established. However, significant deviations from this empirical law were observed for compounds with widely different environments of the investigated atom. Different local symmetries are reflected in different K-edge profiles, which hinder the comparison of the edge shifts [2]. In recent analyses of the average Fe valence in iron gall inks by Fe K-edge XANES spectra large uncertainties in the obtained results are reported [3, 4].

Fe K-edge XANES spectra (Fig. 1) of different standard Fe(II) and Fe(III) iron reference compounds, and of several model iron gall inks with different Fe(II)/ Fe(III) ratio were acquired. The ratio in the latter was also determined using Moessbauer spectroscopy (Fig. 2). X-ray absorption spectra were collected in transmission mode at E4 beamline of HASYLAB synchrotron facility at DESY in Hamburg. A Si(111) double crystal monochromator was used with about 1.5 eV resolution at the Fe K-edge (7112 eV). Equidistant energy steps of 0.3 eV were used in the Fe K-edge scans. Three repetitions were taken to assure the reproducibilty. Exact energy calibration was established with simultaneous absorption measurements on a 5 µm thick Fe metal foil placed between the second and the third ionisation chamber. Absolute energy reproducibility of the measured spectra was ±0.1 eV or better.

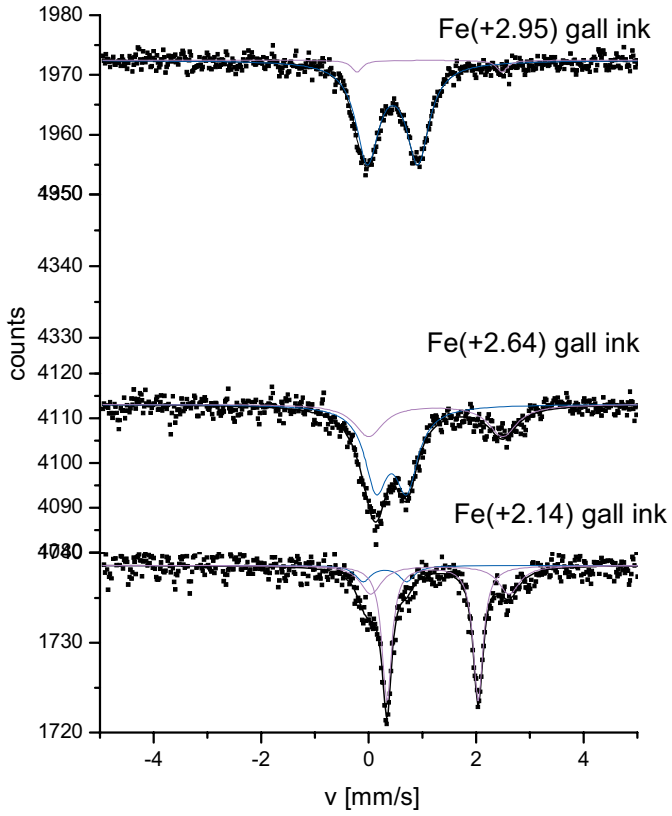

Figure 2: Moessbauer spectra of model iron gall inks on paper (dots) acquired in transmission mode. Fe^{2+} (red line) and Fe^{3+} (blue line) contributions, obtained by a best fit procedure using a standard least-squares fitting routine with Lorentzian lines, are plotted for each spectrum. Number in brackets denotes an average iron oxidation state in a sample

Conclusion

The results show that a proper choice of the Fe reference compounds with same type of atoms in the first coordination shell of Fe ion and similar local structure is crucial for the absolute calibration of the Fe K-edge shift and therewith reliable determination of Fe(II)/ Fe(III) ratio in the sample. In the specific case of iron gall inks, best results are obtained with $FeSO_4 \times 7H_2O$ as a reference for Fe(II) and a model degraded iron gall ink on paper as a reference for Fe(III) XANES spectrum. Using a linear combination fit with these two spectra, it is possible to determine the amount of Fe(II) in the iron gall ink with the accuracy better than 5%.

Acknowledgments

This work was supported by the Slovenian Research Agency research programmes P1-0112 and P1-0153, and by DESY and the European Community under the FP6 Programme "Structuring the European Research Area" contract RII3-CT-2004-506008 (IA-SFS). Access to synchrotron radiation facilities of HASYLAB (project II-04-065) and expert advice on beamline operation by Edmund Welter of HASYLAB is acknowledged.

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NON-CULTIVABLE MICROORGANISMS INVOLVED IN BIODETERIORATION OF HISTORIC PAPER MATERIAL: A CASE STUDY

Astrid Michaelsen [1], Flavia Pinzari [2], Katrin Ripka [1], Werner Lubitz [1], Guadalupe Pinar [1]

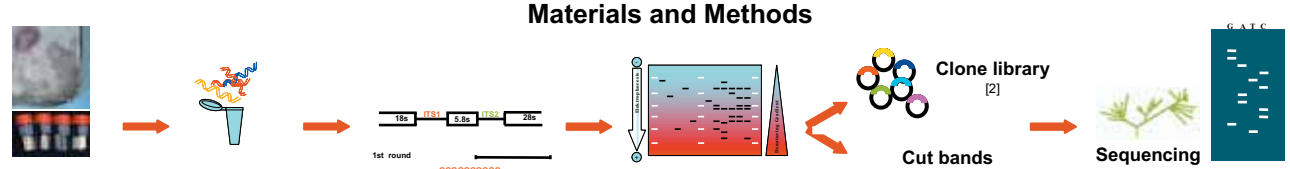
[1] University of Vienna, Department of Medicinal Chemistry, Vienna, Austria
[2] Istituto Centrale per la Patologia del Libro, Laboratorio di Biologia, Rome, Italy

Introduction

The microbial degradation of historic paper is one of the most unappreciated and serious reasons for damage to libraries and archived materials. With the hitherto used conventional methods that rely on culture isolation and subsequent observations of morphological traits, only a small amount of effectively paper colonising microorganisms is detected. Molecular approaches have been developed for the assessment of microbial diversity in complex communities and already applied for objects of art as wall paintings or historic window glass [1,2]. Nucleic-acid-based strategies targeting rRNA-encoding regions offer the potential benefits of a highly sensitive and rapid detection. In this study, for the first time culture-independent molecular methods were used for essays studying the community structure of fungi and bacteria on biodeteriorated paper. A manuscript dated back to 1293 from the archive of La Spezia, made with paper coming from Spain (Fig.1a,b) consisting of cellulose and linen with starch as filling powder, was selected for detailed phylogenetic analysis using cloning strategies. Previous classic cultivation and SEM observations (Fig.1c) did not lead to an identification of the origin of the deterioration phenomena. Illuminated microscopic examination of adhesive tape samples taken from the paper surface lead to the detection of unknown fungal structures (Fig. 1d).

Fig 1. Deterioration of a manuscript from the archive of La Spezia, made with paper coming from Spain (a,b) SEM analysis showed a deep alteration of the structure of the fiber (d).

Materials and Methods



Sampling
~0.5cm² prewashed sample or swab material

DNA extraction
combination of Objects-of-Art-preparation [2] and FastDNA Spin Kit for Soil (Qbiogene)

Nested PCR
[1,3,4]

DGGE
[4,5]

Sequencing + Phylogeny
[2]

Results and Discussion

DGGE analysis revealed fingerprints for both bacterial and fungal communities. Sequence analysis confirmed for the first time the existence of fungi and bacteria on different paper material that could not be cultivated with traditional methods (Fig 3A). A book dating back to 1293 was sampled and used to construct a clone library. By sequencing selected clones from the existence of 9 different bacterial species as well as 8 fungal species could be determined (Fig. 2B, Tab.1). *Aspergillus nidulans*, *Aspergillus penicilloides* and *Alternaria tenuissima* could be defined as paper or gluing spoilers, while *Cladosporium sphaerospermum* can be mostly considered an airborne contaminant since it is often found in dust covering materials. *Chrysomphalina chrysophylla* is not commonly found on library materials. *Wallemia*, *Rhodotorula* and *Aspergillus penicilloides* are usually underestimated among library materials spoilers since they are xerophilic and very slow growing but can be responsible for material degradation. Among bacteria, some species belonging to the genera *Bacillus*, *Stenotrophomonas* and *Kocuria* can potentially spoil the paper because the starch gluing represents a palatable substrate for them. *Shigella*, *Clostridium* and *Caryophanum* can be originated by the usage of the book since these can be human inhabitants and pathogens. The identification of the paper-colonising microorganisms by using molecular methods leads to a better understanding of the current state of historic paper materials, facilitating the prevention, conservation and even restoration. This methodology seems to overcome problems like culture limitations, non-living material or destructive sampling.

Domain	Clone	Strain	Identity [%]
Bacteria	B2	*Caryophanum latum*	96.34
	B4	*Acinetobacter junii*	99.23
	B8	*Shigella sonnei*	98.78
	B14	*Virgibacillus picturae*	95.68
	B18	*Thermophilic bacterium*	90.78
	B21	*Kocuria sp.*	98.89
	B27	*Stenotrophomonas maltophili*	99.69
	B29	*Bacillus piliformis*	93.89
	B31	*Bacillus methanolicus*	96.84
Fungi	F3	*Aspergillus penicilloides*	97.59
	F4	*Chrysomphalina chrysophylla*	73.71
	F8	*Aureobasidium pullulans*	100.00
	F12	*Wallemia sebi UAMH7*	100.00
	F25	*Cladosporium sphaerospermum*	95.64
	F28	*Rhodotorula aurantiaca*	100.00
	F37	*Aspergillus nidulans*	98.57
	F42	*Alternaria tenuissima*	99.52

Table 1. Fungal and bacterial species as determined through sequence analysis performing FASTA search.

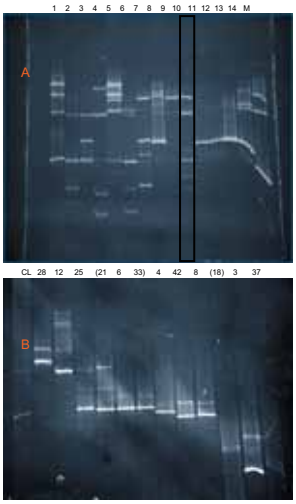


Fig.2. (A) DGGE fingerprints of the ITS1 amplified fragments of fungal communities colonising historic paper samples on a gel containing a denaturing gradient of 30-50% urea and formamide run over 14 h at 100 V. Sample number 12 (lane 10) dated back to 1293 from the archive La Spezia was chosen for cloning strategies. (B) DGGE screening of selected clones derived from sample 12 containing fungal-ITS1 amplified fragments.

Acknowledgement
This work and Astrid Michaelsen were granted by the Austrian Science Fund (FWF) in the frame of the project P17328-B12 " Microbial Colonisation of Paper and Parchment".

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Molecular tools to identify non-cultivable microorganisms involved in biodeterioration of historic paper material

Astrid Michaelsen[1], Flavia Pinzari[2], Katrin Ripka[1], Werner Lubitz[1] and Guadalupe Pinar[1]

[1] Department of Medicinal Chemistry, University of Vienna, Austria
[2] Istituto Centrale per la Patologia del Libro, Italy

Key words: Biodeterioration, paper material, microbial communities, ITS, 16S rRNA gene, DGGE

Introduction and content

Deterioration of cultural objects of art and writs is besides environmental reasons caused by microorganisms. It is also suggested that contamination can occur during paper making or book preparation and not only due to airborne fungi [1]. Archives, collections and libraries suffer from biodeterioration phenomena, but with the hitherto used conventional methods that rely on culture isolation and subsequent observations of morphological traits, only a small amount of effectively paper colonising microorganisms is detected. Many studies on the role of microorganisms in the defacement of cultural heritage utilise standardised laboratory models to establish which species of fungi or bacteria colonise a given substrata, and therefore do not raise the problem of working with objects of art that cannot be cut, sampled, or subjected to invasive analysis. However, when a biology laboratory is asked to supply a purely diagnostic explanation for a degradative phenomenon occurring in a precious art work, the challenge of obtaining an informative sample from the object without damaging it becomes a real operative problem. To this should be added the problem of the viability of micro-organisms and their culturability, which often makes the diagnosis a matter of sheer luck. In fact, as established in environments other than cultural heritage components, the microbial communities found are much more complex and biodiverse than would appear according to classic culturing methods. Microbial investigations based on cultivation strategies cannot be regarded as being reliable in terms of reflecting the microbial diversity present in art works samples. It has been estimated that only about 5% of fungal species have been accurately described due to culture limitations, misidentifications and unexplored habitats [2]. In recent studies nucleic-acid-based strategies targeting ribosomal RNA-encoding regions offer the potential benefits of highly sensitive and rapid detection of microorganisms [3, 4, 5]. The rRNA genes are well suited for analyzing microbial diversity, because they are present in all known organisms, contain conserved as well as variable regions and their sequences are collected in large public databases [6]. Previous research has shown that the variable non-coding internal transcribed spacers (ITS) of the nuclear rRNA genes are better targets for the molecular analysis of fungal communities than the 18S rRNA genes [7, 8]. They are nested between the 18S and the 5.8S nuclear rDNA repeat of the eucaryotic genome. ITS regions provide with a greater taxonomic resolution for fungi than coding regions and they benefit from a fast rate of evolution which results in higher variation in sequence between closely related species, in comparison with the more conserved coding regions of the rRNA genes [9]. Therefore, this methodology has been selected to study the community structure of fungi and bacteria colonising biodeteriorated paper. In the present study, we performed a DNA extraction protocol which allowed the direct extraction of PCR-amplifiable DNA from samples derived from deteriorated paper materials. The crude DNA extracts were used to amplify the ITS1 region. In parallel, the 16S rRNA gene was amplified to obtain a phylogenetic identification of bacteria [10]. The amplified ITS and 16S ribosomal fragments were subsequently analysed by Denaturing Gradient Gel Electrophoresis (DGGE) [11]. Predominant bands were directly sequenced and clone libraries containing PCR fragments

of the ITS region as well as of the ribosomal gene were constructed and clones were screened by DGGE with final sequencing. Initial sequence data base search was performed by the SIMILARITY-RANK tool of the RDP and the FASTA search option [12]. By using this molecular strategy, deterioration spots on historic paper material were investigated for bacterial and fungal colonisation. The selected paper material displaying different deterioration phenomena and foxing spots was previously tested for both fungal and bacterial existence using culturing methods and microscopy. Illuminated microscopic examination of mounted slides carrying adhesive tape samples taken from the paper surface lead to the identification of unknown fungal structures. When micro-invasive sampling is necessary, the use of such very small samples must be optimised to obtain informative results. But in some samples both classic culturing and SEM observations cannot lead to an identification of the responsible for the deterioration phenomena. Using the typing method DGGE revealed fingerprints for both bacterial and fungal communities and sequence analysis confirmed for the first time the existence of fungi and bacteria that could not be cultivated with traditional methods. A selected book obtained from a Spanish library dating back to 1293 was sampled and used to construct a clone library to obtain a detailed phylogenetic identification of the colonising microorganisms. The sample consisted of cellulose and linen with starch as filling powder and the material was dramatically felted and in a bad condition. By sequencing selected clones the existence of bacterial species as *Caryophanum latum*, *Acinetobacter junii*, *Bacillus piliformis / Clostridium piliforme*, *Virgibacillus picturae*, *Shigella sonnei*, *Stenotrophomonas maltophili*, *Thermophilic bacterium*, *Bacillus methanolicus* and *Kocuria sp.* could be proved. The fungal species *Rhodotorula aurantiaca*, *Wallemia sebi UAMH7*, *Cladosporium sphaerospermum*, *Chrysomphalina chrysophylla*, *Alternaria tenuissima*, *Aspergillus penicilloides* and *Aspergillus nidulans* could be determined through sequence analysis. Among these strains, some could be defined as paper or gluing spoilers, like *Aspergillus nidulans, Alternaria tenuissima, Aspergillus penicilloides* while *Cladosporium sphaerospermum* can be mostly considered an airborne contaminant since it is often found in dust covering materials. *Chrysomphalina chrysophylla* is not commonly found on library materials while *Wallemia* and *Rhodotorula* are species that are difficult to be cultured but can be responsible for material degradation. *Wallemia* and *A. penicilloides* are usually underestimated among library materials spoilers since they are xerophilic and very slow growing, and therefore they are hardly detected on common agar mediums. Among bacteria, some species belonging to the genera *Bacillus, Stenotrophomonas* and *Kocuria* can spoil paper, but the presence of bacteria is probably due to starch gluing that represents a palatable substrate for them. Some of the bacteria found on paper can be originated by the usage of the book since these can be human pathogens or inhabitants (*Shigella, Clostridium, Caryophanum*).

European dimension

A fruitful collaboration between our working group and the Laboratory of Biology of the "Istituto Centrale per la Patologia del Libro" (ICPL) in Rome, Italy, has been established to achieve the optimum standardisation of molecular methods on library material. The Institute's chief function is to carry out research aimed at the study from biological, chemical and physical point of view of the deterioration phenomena in library materials, and of the innovative methods for protection, restoration and conservation of ancient and modern books.

Innovation and originality

In this study, for the first time culture-independent molecular methods are used to investigate microbial communities colonising historic paper material of different age and quality. This approach seems to overcome some important problems as culture limitations or destructive sampling and offers the potential benefits of highly sensitive and rapid detection of microorganisms.

Impacts

The benefits expected out of this project are: I) to have a better understanding of the complexity of the microbial communities colonising valuable archival works, as paper and parchment. II) The creation of a catalogue of the microorganisms associated to different deterioration phenomena with special interest in foxing. III) The monitoring of the microflora colonising deteriorated paper samples before and after different restoration treatments with the consequent assessment of a selected restoration method and their validation. These results will be relevant for the efficient preservation of Austrian Cultural Patrimony and can be extended to other European countries with the consequent cultural and economical relevance.

Acknowledgement

This work was supported by the Austrian Science Fund (FWF) in the frame of the project P17328-B12. We are grateful to Dr. Flavia Pinzari from the ICPL in Rome, Italy for providing artificial and real samples, information and support and to Mag[a] Andrea Steitz from the "Holzforschung Austria" for providing us pure fungal material.

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European project details

Austrian Science Fund (FWF), P17328-B12, Microbial Colonisation of Paper and Parchment, Dr. Guadalupe Piñar, 6813 Restoration/Conservation (40%), 1411 Molecular Biology (40%), 1410 Microbiology (1710, 4413) (20%).

DAMAGE ASSESSMENT IN MODEL AND HISTORICAL TAPESTRIES BY FOURIER TRANSFORM IR SPECTROSCOPY (ATR-FTIR)

M. Odlyha, C. Theodorakopoulos, and R. Campana

School of Biological and Chemical Sciences, Birkbeck College, University of London, UK

Tapestries woven in renowned European centres during the 15th-17th centuries are jeopardized by the degradation processes occurring in the coloured wool and silk threads, and at times in combination with metallic threads. The overall aim of the EC-funded project "Monitoring of Damage to Historic Tapestries" (MODHT EV4K-CT-2001-00048) was to develop procedures for recognising tapestries at risk and to provide analysis for informing collection care, which includes their display,storage conditions, and conservation treatment. We propose a damage assessment procedure for woollen threads based on Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR/FTIR) as used for semi-quantitative assessment of chemically modified surfaces in woollen textiles [1,2]

Washing of the tapestries in 17th cent in the Manzanares river (Spain) during the summer period (courtesy C.Carretero Herrero,Palacio Real,Madrid)

Sampling from a historical tapestry at Hampton Court Palace, London (2003)

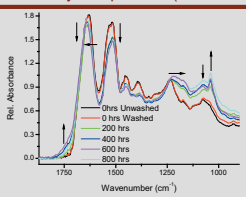
"Dedalus and Icarus" (c.1545), Royal Palace in Madrid with marked locations from wheresample threads were removed at the rear side (image courtesy of M.Hacke, University of Manchester).

Model tapestry fabrication after traditional wool dyeing

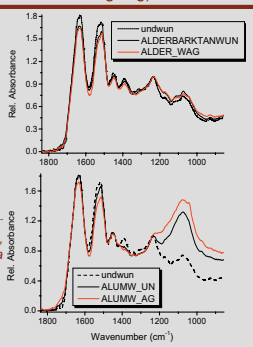
The preservation state of tapestries depends on their past handling and conservation treatment. For the MODHT project, samples were removed from the back of the tapestries where loose threads left by weavers enabled samples to be taken without disrupting the weave structure. Comparison of their state of preservation, as determined from ATR-FTIR, to model undyed and dyed tapestries (before and after accelerated ageing) was made.

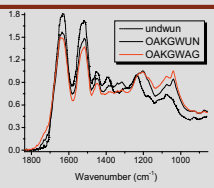
The SensIR® Technologies Durascope attachment for non destructive ATR-FTIR analysis.

The IR beam is reflected onto the sample through a ZnSe crystal



ATR-FTIR spectra in the spectral region 1800 cm-1 –800cm-1 of undyed wool after receiving 30, 60, 90 and 120 Mlux.hrs (light dose). The spectra were normalised at amide III (1232 cm-1).

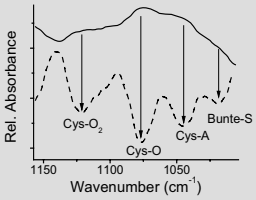




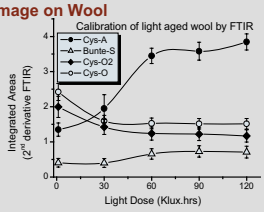
Effects of mordants on the degradation of wool: Alder bark does not affect the wool and may have antioxidant protective properties since there is no Cys-A increase after light exposure (60Mlux.hrs). In contrast Oak gall mordant is a strong oxidising agent. In the case of alum $Al_2(SO_4)_3$, the Al-O stretching vibration obscures the fingerprint region.

As part of our contribution to the MODTH project we studied model and historical wool samples using the Durascope equipped with a ZnSe crystal, in the sample compartment in the Perkin Elmer FTIR 2000. The spectral region of interest occurs below 1150 cm-1 and includes absorbances of cystine monoxide (1071 cm-1), cysteic acid (1040 cm-1) and S-sulphonate or Bunte salt (1022 cm-1) [1.2]. In the model tapestries it was the oak gall mordant and the black dyed samples (FeSO4/oak gall) that showed the highest value for the cysteic acid peak and the highest value for oxidative damage before accelerated light ageing.

2nd Derivative FTIR Quantification. Cys-A index: A Marker for Oxidative Damage on Wool

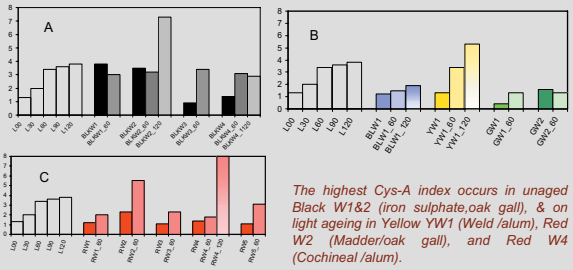


The increase in absorbance in the cysteic acid peak during light ageing is more clearly seen in second derivative FTIR. Peak area measurements were made and plotted vs light dose (next figure).



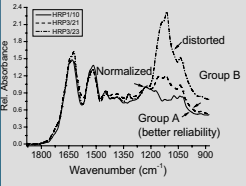
The cysteic acid signal increased with received light dose up to 60Luxhrs and then the rate of change decreased. It was chosen as a marker to represent the oxidative damage in model and historical wool samples

The three figures show the plot of Cys-A (from FTIR) vs sample type. The effect of light ageing on the undyed sample is shown on the left of each of the 3 graphs and the effect of light ageing on(A) black, (B) yellow,blue,green and (C) red dyed samples is also shown.



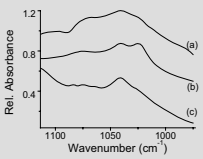
The highest Cys-A index occurs in unaged Black W1&2 (iron sulphate,oak gall), & on light ageing in Yellow YW1 (Weld /alum), Red W2 (Madder/oak gall), and Red W4 (Cochineal /alum).

ATR- FTIR Historical Wool Sample Evaluation.

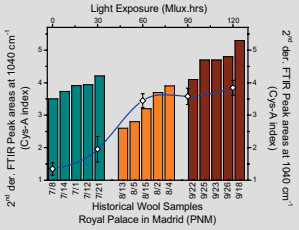


The majority of historical samples, were similar to the model samples (Group A). However,some historical wool samples had high absorbances in the fingerprint spectral region below 1150 cm-1. This could be due to incorporated dust particles and/or degradation products (Group B).

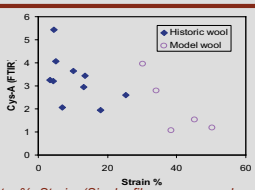
Historical samples in group A were separated into 3 distinct categories, i.e. cases with clear absorbance peaks of: (a) cystine S-monoxide, cysteic acid and no cysteine S-sulphonate



residues, (b) less cystine S-monoxide, cysteic acid, and cysteine S-sulphonate (c) and cysteic acid as the major product.



Cys-A indices of wool samples from historical tapestries plotted with the Cys-A index plot for undyed light aged samples.



Cys-A to % Strain (Single fibres measured on Instron tensile tester). [Mechanical data from M.Hacke, University of Manchester]. Cys-A for historical and accelerated aged samples are higher than for unaged (Cys-A between 1 and 2). Historical samples have lowest % strain values.

This work shows that there is a rapid and accurate way to assess the degradation of historical tapestries by providing a Cys-A index from 2nd derivative FTIR that is associated with the oxidative state of the material but most significantly with the strength of the woollen threads.

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MODHT EVK4-CT-2001-00048

Acknowledgements: European Commission 5th Framework Environment Programme (section 4.2.1 Improved Damage Assessment of Cultural Heritage)

Damage assessment in model and historical tapestries by fourier transform infra-red spectroscopy (ATR-FTIR)

M. Odlyha, C. Theodorakopoulos and R. Campana

School of Biological and Chemical Sciences, Birkbeck College, University of London, UK

Key words: tapestries, wool, cysteic acid, 2nd derivative FTIR spectroscopy

Introduction and content

Tapestries woven in renowned European centres during the 15th to the 17th centuries are among the most valuable testimonies of European cultural heritage. Their survival is jeopardized by the degradation processes operating in the coloured threads (wool and silk) and the metal threads. The overall aim of the EC-funded project "monitoring of damage in Historic tapestries" (MODHT EV4K-CT-2001-00048) was to develop procedures for recognising tapestries at risk and to provide analysis for informing collection care, and this includes their display and storage conditions, and their conservation treatment. The project brought together conservators-restorers, curators, conservation scientists and scientists and it was also the first time that a comprehensive interdisciplinary study was made using complementary analytical techniques [1] Part of our contribution in the MODHT project was an assessment of damage in woollen threads, which can be indicative of the state of preservation of the tapestries from which they originate. This was provided by Attenuated Total Reflection – Fourier Transform Infrared Spectroscopy (ATR/FTIR). A series of undyed and dyed model tapestries were initially assessed and the results were used for comparison with woollen threads sampled from 13 historical tapestries (Figure 1).

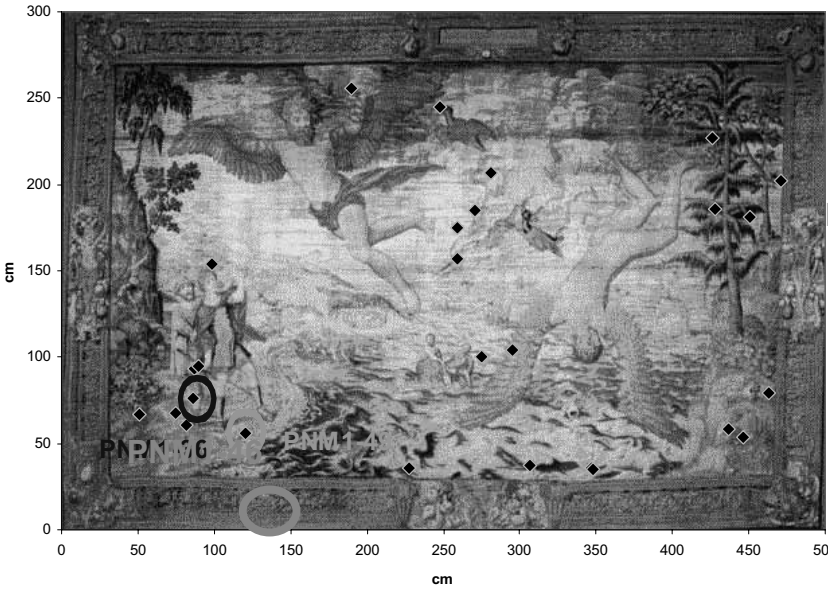

Figure 1: Tapestry "Dedalus and Icarus" (1545) from the collection in the Royal Palace, Madrid. Marks indicate locations of sampling of metal threads (A.M. Hacke) (University of Manchester [2])

European dimension

This is the first EC-funded project which focuses on damage assessment in tapestries. The project realised an interdisciplinary approach using advanced and complementary analytical techniques. Specialist expertise from various European laboratories made the following possible: (1) the preparation of model tapestries, woven and dyed according to traditional procedures (University of Manchester, Textiles and Paper Dept. and the Royal Institute for Cultural Heritage, Brussels), the analysis of dyes (Royal Institute for Cultural Heritage, the National Museum of Scotland and the University of Edinburgh), (3) characterisation of woven textile according to (a) mechanical properties and (b) alterations with preparation and accelerated ageing by chromatographic, spectroscopic, X-ray analytical techniques, scanning probe microscopies, and comparison with state of degradation of historical samples (Hampton Court, Conservation Dept., Birkbeck College, London, and University of Manchester).The project has provided an analysed set of model samples (total of 22 wool and 19 silk) undyed, dyed (14 different dyes and three mordants), and accelerated light aged samples. This provides a valuable repository of samples which can be made available to future projects. Damage assessment procedures were developed on the model threads and the modified analytical procedures were then applied to the historical threads. In the course of these studies it was found that dyeing processes cause damage to the threads [5]. It was also possible to assess damage in historical samples and compare this with the light aged samples.

Innovation and originality

Previous work has shown that the state of preservation of woollen threads could be monitored by following the changes in intensity of the cysteic acid peak at 1040 cm^{-1}[3]. This is formed from the oxidation of cystine residues which play an important part in stabilising the wool's fibre structure. Prior work on wool degradation demonstrated the possibility of semi-quantification of the state of degradation in wool using 2nd derivative FTIR [3, 4]. Evolution of cysteine S-sulphonate (Bunte salt) at 1022 cm^{-1}, was also monitored (Fig. 2).

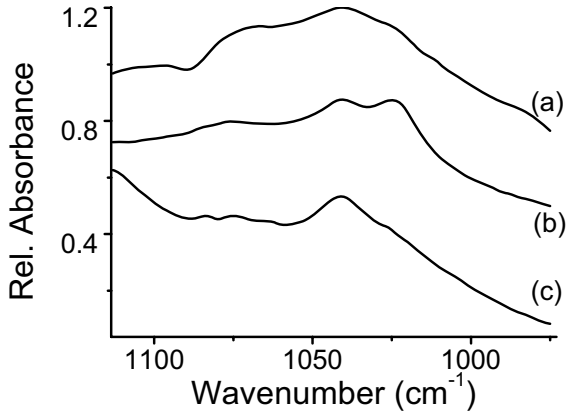

Figure 2: ATR-FTIR spectra show the increase in the ~1040 cm^{-1} peak, due to cysteic acid, and the presence of ~1020 cm^{-1} peak due to cysteine S-sulphonate (Bunte salt). Samples shown are: (a) PNM8/13 (b), BRU1/10 (c), PNM9/18 from collections in Spain (a)(b) and Belgium (c)

Quantification of the cysteic acid increase was performed using 2nd derivative FTIR spectra, which were previously normalised at amide III peak (1232 cm^{-1}). The results were in a good agreement with tensile strength tests which showed that the increase in cysteic acid reduced significantly the strength of the samples [5]. Data from historical samples also showed correlation between tensile strength measured on single fibres and presence of cysteic acid [M. Hacke private communication]. In unaged model tapestries it was observed that oak gall

mordant, used in the dyeing process, damaged the wool. For alum mordanted only samples $Al_2(SO_4)_3$, the cysteic acid peak is obscured by contributions from the mordant alum, and so the damage could not be assessed by ATR-FTIR. The effect of various dyes including madder, brazilwood, cochineal, woad did not lead to a significant increase in cysteic acid. The black dyed unaged samples (oak gall with $FeSO_4$), however, showed an increase in the presence of cysteic acid. Further damage on accelerated light ageing was measured, particularly in the yellow (weld / alum) and red (madder / oak gall) samples. The majority of the historical samples had similar FTIR spectra to the accelerated light aged model samples. However, there were samples with high absorbances in the fingerprint spectral region (below 1150 cm^{-1}) In such case the part of the spectrum containing the cysteic acid absorption was somewhat distorted and despite the ability to provide clear Cys-A index calculation it was decided not to compare such results with the those coming from samples with a better resolved fingerprint region (below 1150 cm^{-1}). Among the selected samples there were three distinct categories based on the spectral shape of the fingerprint region; (a) cystine S-monoxide, cysteic acid, and no cysteine S-sulphonate residues, (b) cysteic acid and cysteine S-sulphonate residues and (c) cysteic acid as the major product. Despite these differences all peaks and especially the one corresponding to cysteic acid were measurable with clear wavenumber limits in the second derivative spectra.

Impacts

The most significant impact so far has been the interaction with the Infrared and Raman Users' Group. This involves conservation scientists and conservators-restorers from major museums and art galleries. Part of their activity is maintaining a large database of spectra from cultural objects. They are also interested in our contribution to this database. In addition there is also interest in the repository of samples in the MODHT project. It is recognised that there is a lack of historical material and also model samples prepared according to traditional practices. In many cases method development is in progress. Availability of samples is considered of vital importance, in particular of historical threads still remaining from the project. As spectral techniques are non-destructive samples will form a useful set for spectroscopic investigations.

Acknowledgements

The authors are grateful to the European Commission DG-RTD 5th Framework "City of Tomorrow and Cultural heritage" for funding the MODHT project (contract no. EV4K-CT-2001-00048). We also thank our partners in the MODHT project, in particular Prof. C. Carr (University of Manchester) for advice on derivative FTIR, Marei Hacke (University of Manchester) for tensile testing of single wool fibres, and Kathryn Hallett for tensile testing of woven model tapestries.

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European project details

This work was performed in the framework of the EC-funded project "Monitoring of Damage in Historic Tapestries" MODHT (Contract no. EVK4-CT-2001-00048) Professor C. Carr Dept. Textiles and Paper, University of Manchester C58 Sackville St. Building, Manchester, UK.

Heat flow measurements on historical materials

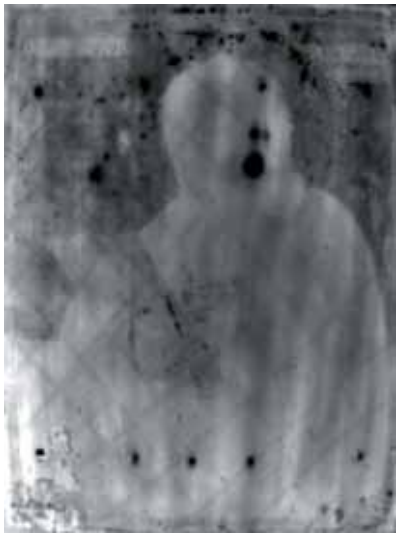
Peter Meinlschmidt[1], Jochen Aderhold[1], Volker Märgner[2]

[1] Wilhelm-Klauditz-Institut, Fraunhofer-Institute for Wood Research, Braunschweig, Germany
[2] Braunschweig Technical University, Institute for Communications Technology, Germany

Infrared Techniques make invisible defects and traditional art techniques visible.

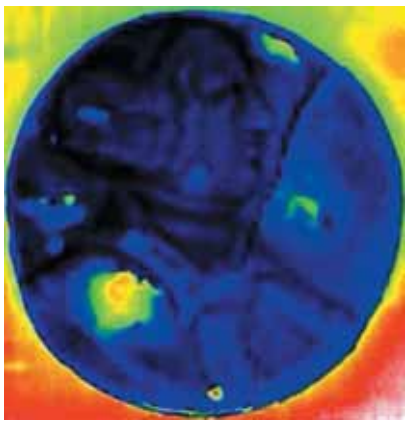
Object: Historical wood paintings (icons)

Detected defects:
Replaced paint
Screws & nails
Knots
Wood treatment
Insect grooves
Delaminations



Object: Ornamental building material (terra-cotta)

Detected defects:
Replaced paint
Debonded areas
Delaminations



Object: Historical watermarks

Detected defects:
Density changes
Thin material
No interferences
with drawings

Heat flow measurements on historical materials

Peter Meinlschmidt[1], Jochen Aderhold[1] and Volker Märgner[2]

[1] Wilhelm-Klauditz-Institut, Fraunhofer-Institute for Wood Research, Braunschweig, Germany
[2] Braunschweig Technical University, Institute for Communications Technology, Germany

Key words: thermography, infrared, on-line, pulse, transmission, icons, terracotta, watermarks

Introduction and content

The detection of invisible defects like faults, cracks and debondings are important for every restorer while working with historical materials. Only a few techniques can be applied to such sensitive surfaces to get information about the actual condition of the valuable material without touching the material. One contact-less and therefore non-destructive technique is the heat flow measurement using an infrared (thermographic) camera.

European dimension

Most of the historical materials as well as the damages happened to the art objects can be found all over Europe. This increases the need for test methods which can be applied almost everywhere to help the restorers to find hidden defects without touching the historical material.

Innovation and originality

Infrared thermography is a fast and non-destructive testing and evaluation method that can rapidly measure and interrogate large surfaces for invisible defects and structural faults [1-4]. If material under inspection is warmed with radiators, the temperature of the surface will rise suddenly. The speed at which the heat front dissipates into the material depends on the thermal properties like density, heat capacity, thermal conductivity and the bonding quality between top surface layer and the base material. A defect in the sub-surface creates a barrier for the heat diffusion process and, therefore, the surface temperature above the defect will decrease more slowly than the temperature in other regions. The surface above such a defect will show a hot spot on the surface. The principle of this technique is shown schematically in Figure 1.

The detection of defects can take a few seconds or even some minutes after the heat impact depending on the material and depth of the defect.

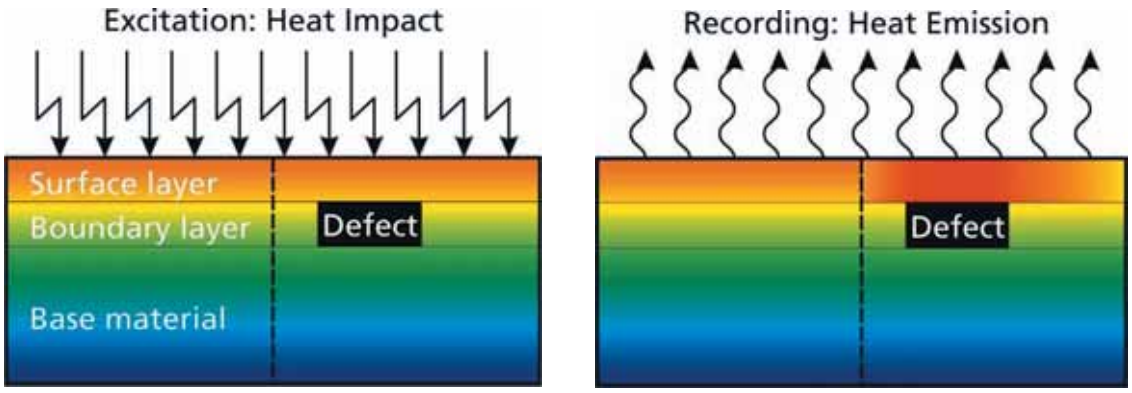


Figure 1: Schematic drawing of thermography, showing the uniformly distributed heat impact on the surface (left), the recorded heat emission (right). Warmer regions (dark) show the defect

For *active on-line thermography* the material under inspection is placed on a conveyor belt that transports the samples along an infrared heat source (Figure 2). The surface is heated homogeneously by a few degrees centigrade. During the further transport the heat penetrates into the material and the infrared camera, which is placed above the conveyor belt, records the temperature on the surface. The used infrared camera with the very high temperature resolution of 0.02 K allows with little heat already the detection of defects and structural faults even deep within the material with high accuracy.

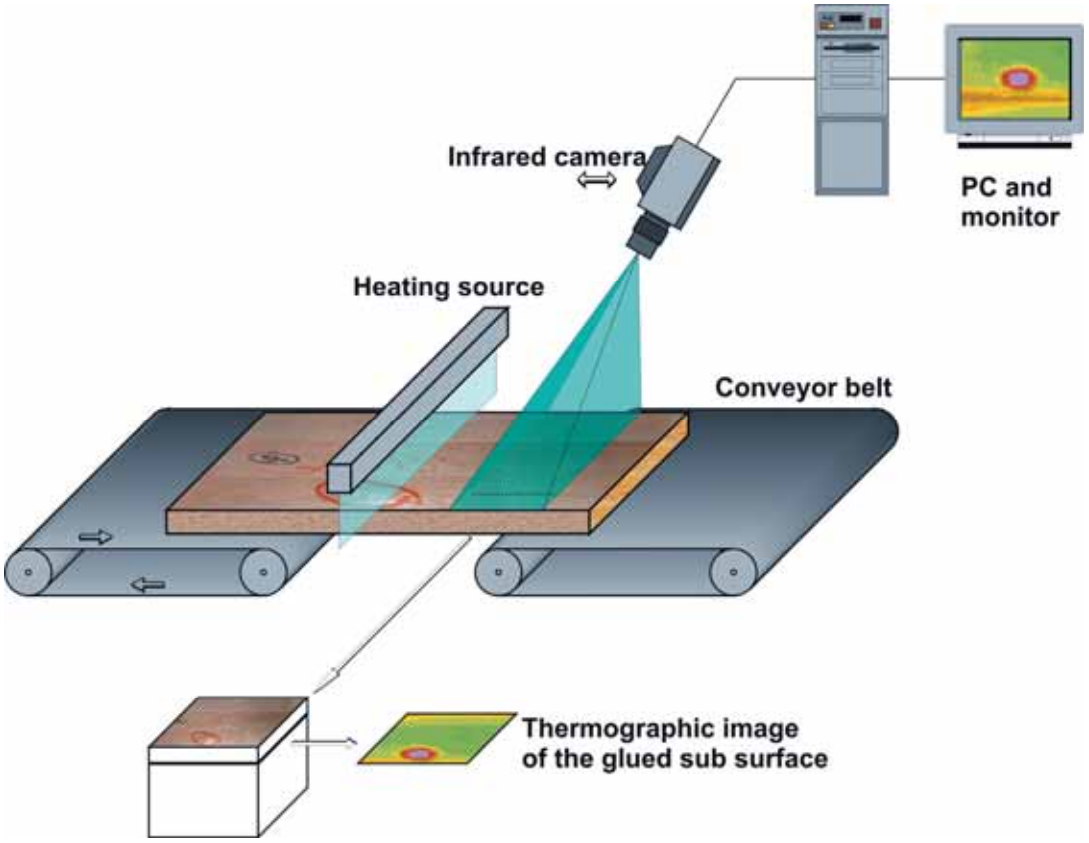


Figure 2: Schematic drawing of the thermographic set-up for the detection of debondings and structural faults within historical material

Impacts

Figure 3, left shows a photo of a historical icon with a painting on canvas which covers a wooden frame. Figure 3, right shows the corresponding infrared or thermal imaging after a short heat impact on the conveyor belt. During this measurement the surface temperature increased about 5 °C.

The thermal image shows clearly the remaining historical real gold (gold leaves) as black or cold areas. Because of the high heat conductivity and capacity, these areas appear colder as the vicinity. The renewed gold colours can be clearly distinguish from the historical gold by its grey colours. Poor bonded regions, insect's burrows and cracks in the surface can be detected as warm / white areas or small white lines. These regions appear white or hotter because of the poor heat conductivity into the base material. The interesting good visible chequered structures are structural faults provoked by the broken canvas which is stretched over the wooden frame.

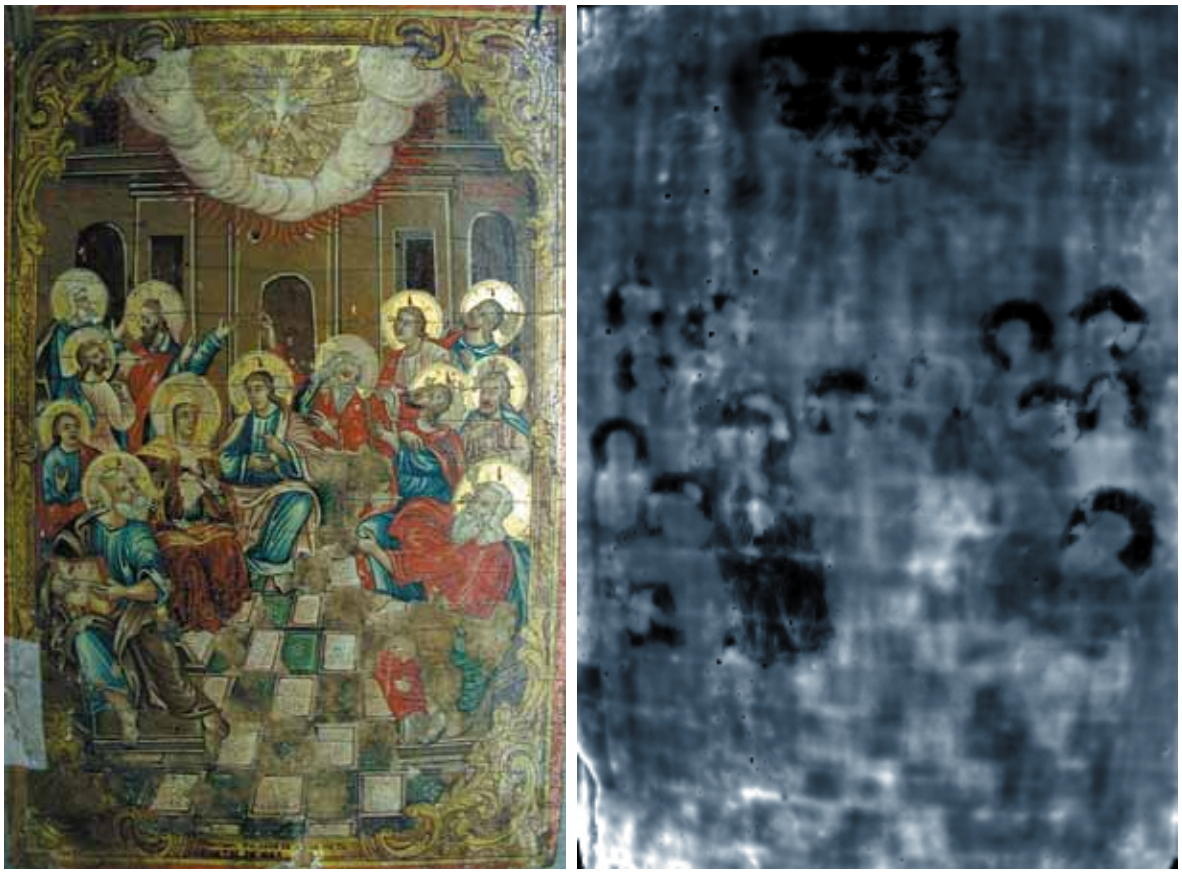


Figure 3: Photo of a historical painting (left and the recorded infrared image (right) Warmer regions are shown in white and colder regions in dark colours

Acknowledgment

This research work was funded, financed and supported by the Wilhelm-Klauditz-Institute and the Braunschweig Technical University.

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Prevention of mould growth by a suitable temperature and humidity regulation strategy

Dipl.-Rest. Univ. Ralf Kilian; Dr.-Ing. Martin Krus; Prof. Dr.-Ing. Klaus Sedlbauer IBP Holzkirchen

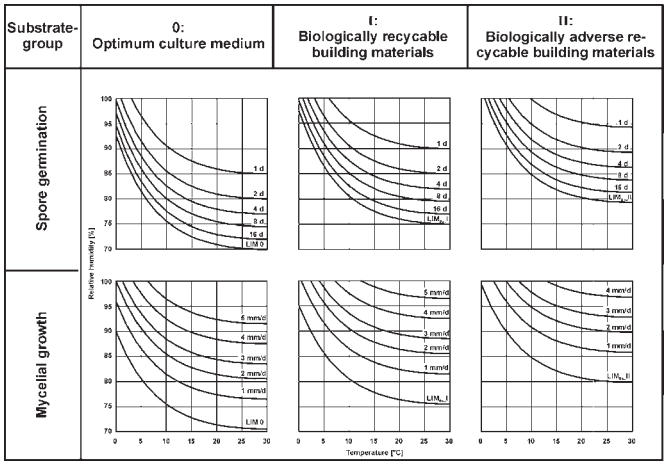
Baroque fresco with mould

Requirements for Mould Growth

Essential for the risk of mould growth are type of substrate, the temperature and transient course of relative humidity on the surface.

The **Generalized Isopleth Systems** show the correlation between R.H. and temperature on spore germination and mycelial growth:

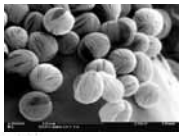
Substrate category 0: Optimal culture medium
Substrate category I: Biologically recyclable building materials
Substrate category II: Biologically adverse recyclable building materials

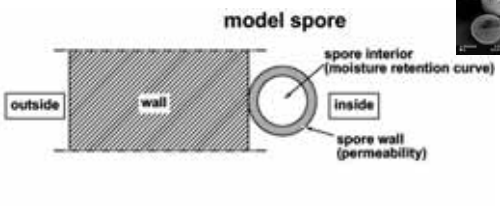


Biohygrothermal Model (WUFI® Bio)

For the consideration of real ambient conditions the moisture behaviour of the spore is calculated.

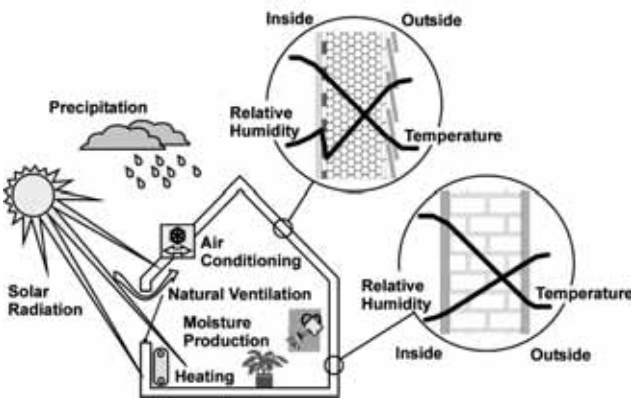
The exceedance of a critical water content depending on temperature means that the germination process has been completed and mould growth is starting.

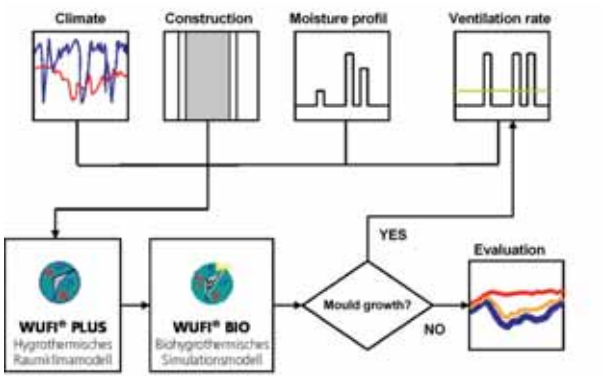




Whole Building Mode (WUFI® Plus)

With this hygrothermal model of the building construction, the interaction of inside materials, the moisture production, the ventilation rate and the inside climate can be simulated.





Combining Both Models

By combination of the biohygrothermal model with the whole building model it is possible to obtain a climatization strategy for a specific building. It enables a secure prevention of mould growth with a minimisation of energy losses and indoor climatic changes.

Responsible editors: Dipl.-Restaurator Univ. Ralf Kilian, Dr.-Ing. M. Krus
IBP Holzkirchen, Department of Indoor environment, climatic impacts

Fraunhofer Institut Bauphysik

Fraunhofer-Institut für Bauphysik (IBP)
Directors: Prof. Dr.-Ing. G Hauser, Prof. Dr.-Ing. K. Sedlbauer
D-83626 Valley, Fraunhoferstraße 10, (Postf. 1152, 83601 Holzkirchen)
D-70569 Stuttgart, Nobelstraße 12, (Postf. 80 04 69, 70504 Stuttgart)
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Prevention of mould growth and moisture related damages on indoor cultural heritage by a suitable temperature and humidity regulation strategy

Ralf Kilian, Martin Krus and Klaus Sedlbauer

Fraunhofer-Institute for Building Physics, Germany

Key words: preventive conservation, climate, mould growth, climatisation, ventilation strategies

Introduction and content

It is a well known fact that fluctuating indoor temperature and in a far more serious way fluctuating indoor relative humidity are causing damages to valuable surfaces of works of art like paintings or wooden sculptures. Therefore the best solution may be to keep the relative humidity (r.H.) constant, preferable at about 65% r.H., which is the medium r.H. you will get inside in summertime by opening the windows. On the other side in wintertime with this r.H., depending on the insulation standard of the building, you will run into problems due to surface condensation and mould growth on the outer walls or window frames. This means an acceptable range of r.H. has to be defined, depending on the different materials to be preserved and allowing a damage free use of the building during the whole year. For this a climatisation strategy has to be developed which allows a smooth shift of the r.H. and temperature during the year without a high amount of harmful peaks.

The course of the r.H. is strongly influenced by the buffering effects of the building envelope materials and inside furniture as well as the transient outdoor conditions. For the development of a suitable ventilation and heating system these effects have to be taken into account. A new *whole building model* for the simulation of the heat and moisture transfer effects which influence the indoor climate has been developed and validated recently. A combination of this model and an innovative model for the determination of the risk of mould growth enables us to assess different temperature and humidity regulation strategies for the preservation of indoor cultural heritage.

Innovation and originality

The hygrothermal behaviour of a building component exposed to weather is an important aspect of the overall performance of a building. Today the hygric transport phenomena in the building envelope are well understood and a realistic assessment of all relevant effects can be carried out by one of the numerous models and computer programs that have been developed in different countries over the last years. The calculation of the hygrothermal performance of a part of the envelope is state-of-the-art, but until now the total behaviour of the actual whole building is not accounted for.

Its importance is immanent as historic buildings usually show elevated indoor humidity levels and a high variation of the climatic conditions, which can be dangerous to the cultural heritage materials. This requires the detailed consideration of all hygrothermal interactions between the indoor air, the furnishing and the building envelope. In [1] a new holistic model is presented, that takes into account the main hygrothermal effects, like moisture sources and sinks inside a room, moisture input from the envelope due to capillary action, diffusion and vapour ad- and desorption as a response to the exterior and interior climate conditions. Also different heat

sources and sinks inside the room, heat input from the envelope, the solar energy input through walls and windows as well as hygric and thermal sources and sinks due to natural or mechanical ventilation are considered. This new whole building model WUFI® PLUS is a combination of thermal building simulation and the hygrothermal envelope calculation model WUFI® [2].

How much ventilation and additional heat energy is required to ensure safe indoor conditions for cultural heritage when a building is exposed to additional moisture? What will happen to the hygrothermal behaviour of walls and ceiling when a historic cellar is changed in its use and is turned into a discotheque or restaurant? How do the indoor air conditions and the envelope of buildings with temporary occupation react to different heating and ventilation strategies? Can sorptive finish materials improve human comfort and stabilise the climate in historic buildings? These questions can either be answered with the help of experiments or by numerical simulations. In view of the fact that experiments are often time-consuming and, in some cases, both problematic and expensive, intensive work has been done over the past few years on the development of mathematical approaches and procedures to evaluate the real hygrothermal performance of the whole building. During the last years several models for calculating the thermal behaviour of a building were developed. Nevertheless, most of the commonly used thermal building simulation tools treat the moisture exchange with the envelope in a simplified manner by assigning a certain moisture storage capacity to the interior of the building. This approach is often sufficient as long as average humidity conditions are the only concern. However, if the exact indoor humidity fluctuations or the moisture profiles in the building envelope are relevant, new models that combine thermal building simulation with the hygrothermal component simulation have to be applied.

The only chance for the long term prevention of mould is to ensure that the hygrothermal situation on the surface is not convenient for mould growth. The use of biocides works only for a limited period and may affect health and environment. Up to now the common methods to assess the risk of mould growth are based on steady boundary conditions. WUFI® BIO, a newly developed model describing the hygrothermal behaviour of the spore, allows for the first time to account for the changing surface temperature and R.H. for the prediction of mould growth [3]. The combination of the biohygrothermal model WUFI® BIO with the whole building model WUFI® PLUS enables secure prevention of mould growth together with a minimization of energy losses and indoor climatic changes.

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MONOCHROMATIC LIGHT AND PORTABLE SPECTRORADIOMETRY FOR THE CONSERVATION OF STONE MONUMENTS AFFECTED BY PHOTOTROPHIC MICRO-ORGANISMS

P. ALBERTANO[1], L. BRUNO[1], S. PIERMARINI[2], & S. BELLEZZA[1]

[1]DIP. DI BIOLOGIA & [2]DIP. DI SCIENZE E TECNOLOGIE CHIMICHE, UNIVERSITÀ DI ROMA "TOR VERGATA", Italy.

In the frame of the CATS project involving ten participants from different European countries, a research has been conducted with the aim to investigate epilithic phototrophic biofilms that cause deterioration on stone substrata inside the Roman Catacombs of Domitilla and St. Callistus (Fig. 1 a-b) in Rome (Italy). A multidisciplinary approach was undertaken in order to develop innovative non-invasive methods for the safeguard and monitoring of valuable lithic faces. Part of the project was developed in the Italian laboratories and focussed on: i) the cytomorphological characterisation of the biofilms *in toto* and the phototrophic cyanobacteria present inside them (Figs. 1-2); ii) the identification and testing of monochromatic lights on biofilm development and their "in situ" application (Figs. 3-4); iii) the establishment of a monitoring protocol based on spectroradiometric techniques (Fig. 4). Moreover, to understand the ecophysiology of the phototrophic biofilms and the biogeochemical fluxes that led to the biotransformation and irreversible biomineralisation of lithic faces other non-invasive methods were applied (Fig. 5) based on the use of Pulse-Amplitude-Modulation fluorimetry and elettrochemical microsensors. The results so far obtained allowed the definition of innovative protocols for portable spectroradiometry to reduce and monitor cyanobacterial growth.

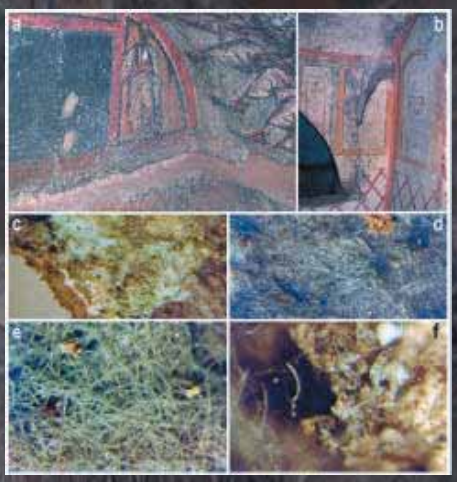


Fig. 1. (a) Detail of the *arcosolium* of the "Cubicolo degli Apostoli Piccoli" at the Catacombs of Domitilla where blue-green biofilms are visible on the bottom right. (b) Frescoes inside the "Cubicolo di Oceano" at St. Callistus catacomb with spotted phototrophic growth. (c) Pale-green patina on plaster formed by Chroococcalean cyanobacteria, actinobacteria and *Scytonema julianum*. (d) *S. julianum*, *Fischerella* sp. and *Phormidium* sp. biofilm. (e) Detail of *S. julianum* calcified filaments on stone surface and (f) inside a micro-gravity. Scale bar 10 μm.

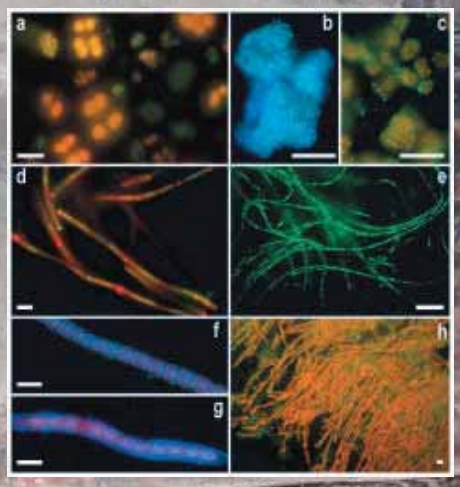


Fig. 2. Epifluorescence was used to characterise viable cyanobacterial taxa within biofilms.

(a) Biofilm dominated by *Gloeothece membranacea* after acridine orange (AO) labelling for nucleic acids (yellow fluorescence) and exopolysaccharides (green fluorescence). *Eucapsis* sp. after DAPI (b), and AO staining (c). *Leptolyngbya* sp. after AO staining of nucleic acids that fluoresce yellow (d) or green (e) depending on the filter set used. DAPI staining of *Fischerella* sp. (f) and *Scytonema julianum* (g). (h) AO staining of *Fischerella* sp. Scale bar 10 μm.

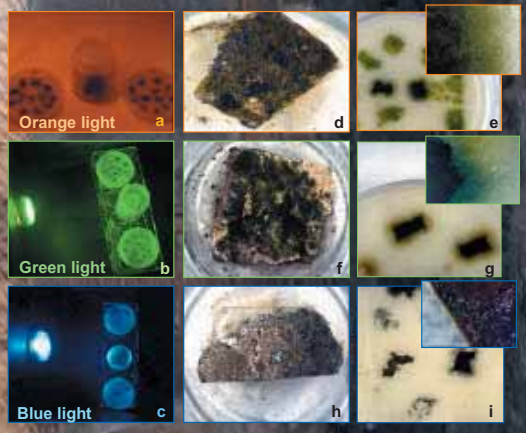


Fig. 3. Biofilms collected *in situ* were inoculated both on calcareous slides from Roman Catacombs (d, f, h) and agarised medium (e, g, i) specific for cyanobacteria and exposed to orange (a), green (b) and blue (c) monochromatic lamps. After 10 months the biofilms under orange light (a, b, c) showed an evident growth on both substrata (d, e), while biofilms grown under green and blue light light were partially (f, g) and fully inhibited (h, i).

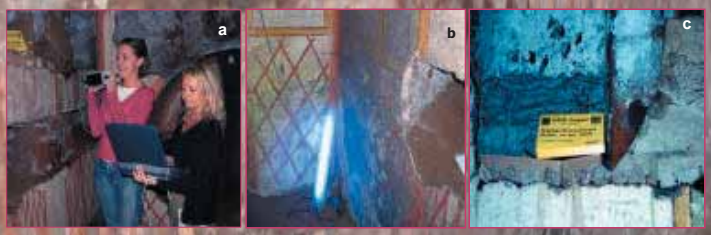
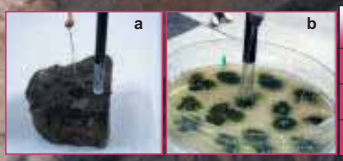


Fig. 4. Spectroradiometric measurements were taken with a portable Ger1500 in order to characterise lamp and biofilm emission in laboratory (see Fig. 3) and *in situ* (a) conditions. After the experimental tests, the blue monochromatic lamp was selected for the installation inside the "Cubicolo di Oceano" in St. Callistus catacomb (b). The biological colonisation of calcareous slides under blue light *in situ* was followed by monthly recording of emission spectra (c). After 12 month monitoring a very scarce growth was detected on slides, mostly due to short *Fischerella* filaments and few associated bacteria.

Therefore, the non-destructive use of the portable spectroradiometer allowed :

- to define the wavelengths emitted by the lamp currently used in the catacombs;
- to select the most appropriate monochromatic light for the experiments;
- to test the efficacy of monochromatic lamps in reducing cyanobacterial development;
- to establish protocols to quantify mean relative growth of cyanobacterial biofilms in laboratory and *in situ* conditions.



Luce	pH ± Std. Err	$[Ca^{2+}]$ mM ± Std. Err
Arancio	7.8 ± 0.2	87 ± 2
Verde	7.3 ± 0.2	46.0 ± 0.2
Blu	6.9 ± 0.1	40.0 ± 0.2

Fig. 5. The combined use of PAM fluorimetry and potentiometric microsensors allowed to evidence a reduced photosynthetic capacity of biofilms under green and blue light. This was reflected by the pH decrease and a reduced mobilisation of calcium ions from the stone substrata. Both methods are non-invasive and have the advantage that can be adapted for measurement on other biofilm types and substrata.

European Project Detalis: CATS project, EESD n°EVK4-CT-2000-00028, "Cyanobacteria attack rocks: control and preventive strategies to avoid damage caused by cyanobacteria and associated micro-organisms in Roman hypogean monuments", Co-ordinator: Patrizia Albertano, Dept. of Biology, University of Rome "Tor Vergata", albertano@uniroma2.it, 5th Framework Programme.

Monochromatic light and portable spectroradiometry for the conservation of stone monuments affected by phototrophic micro-organisms

P. Albertano[1], L. Bruno[1], S. Piermarini[2] and S. Bellezza[1]

University of Rome "Tor Vergata", Dept. [1] Biology and [2] Chemical Sciences and Technologies, Italy

Key words: biodeterioration, cyanobacterial biofilms, lighting systems, control and monitoring

Introduction and content

In archaeological subterranean sites, most of the micro-organisms that colonise exposed stones are transported by air and settle on surfaces where they can grow into biological patinas, the biofilms, in presence of suitable environmental conditions [1, 11]. In the last years, a project was conducted to investigate epilithic phototrophic biofilms that grow on stone substrata of historical and artistic value from the ecological, morpho-functional, genetical, biochemical and taxonomical point of view, and to develop innovative methodological approaches for safeguard and monitoring of valuable lithic faces [4]. Part of the project was developed in the Italian laboratories and particularly devoted to the following objectives: I) to characterise phototrophic biofilms and the microenvironment in which they develop, and to describe cytomorphology, ecophysiology, biochemistry and genetics of component micro-organisms and isolates grown in laboratory controlled conditions; II) to identify and test monochromatic lamps able to interfere with cyanobacterial growth for control or prevention of phototrophic biofilm development; III) to test and define monitoring methods based on portable spectroradiometry. On these bases, several cyanobacterial species were detected in Roman catacombs and other hypogea together with few taxa of eukaryotes to which abundant populations of heterotrophic bacteria were associated [9, 10, 12, 14, 16, 22]. Thanks to a polyphasic approach it was possible to identify either airborne bacteria or phototrophic prokaryotes, microalgae and fungi in epilithic biofilms, and to evidence tight relationships between cyanobacteria and bacteria [19-21]. The peculiarity of the hypogean environment was described as well as its interactions with the biological community and the colonised substrata [1, 17, 18]. The identification and characterisation of deteriogenic mechanisms affecting stone was also achieved trough the development of microsensors to understand biogeochemical fluxes and biofilm functioning that led to the biotransformation and irreversible biomineralisation of lithic faces [4, 7, 8, 17]. In addition, the response to different monochromatic blue and green lamps was tested to establish protocols useful for limiting cyanobacterial development, and non invasive methodological approaches based on portable spectroradiometry were developed for the monitoring and control/prevention of growth of phototrophic biofilms on stone [2, 3, 6, 15].

European dimension

The project included the collaboration between nine groups of Italian, British, Finnish, German and Spanish researchers with expertises in microbiology, biotechnology, botany, analytical chemistry, mineralogy, archaeology, conservation and management of cultural heritage plus the involvement of an Italian SME expert in sensor technology. This collaboration resulted in the definition of innovative portable equipment and protocols for best practices that can open new market possibilities for industrial and commercial exploitation.

Innovation and originality

Up to date, most of the strategies applied in the conservation of lithic surfaces against biologically caused decay have been using large-spectrum toxic chemical compounds. The use of harmful compounds represents a real risk for the environment and people working directly or indirectly with them. The application of physical methods based on illumination system providing appropriate wavelengths will reduce the use of toxicants and improve health and environmental safety. In addition, the testing of acceptability of this innovative approach was conducted on the visitors of one catacomb in Rome to assess the interest and the positive attitude of the public to the adoption of new strategies for the conservation of cultural heritage [5]. The development of alternative methods for a better preservation and management of cultural properties, and the assessment of the risks connected to the biological deterioration of lithic surfaces also addressed the issue of the *in situ* monitoring of phototrophic biofilms through a non-invasive technique.

Impacts

The use of the proposed anti-cyanobacterial strategy was never attempted before and its application as an alternative physical method to prevent or reduce biofilm formation represents a useful approach for the conservation of confined sites with high humidity and flux of visitors. The development of methods that are not harmful to the environment and human health was paralleled by basic studies on phototrophic biofilms that contributed to increase knowledge of (new) organisms and addressed the issue of preservation of environmental biodiversity in archaeological hypogea. Several species were in fact described from this environment for the first time and a large number of clonal of phototrophic and heterotrophic bacteria were isolated as potential source for new biomolecules and future genetic resources. Besides the end-users directly involved in the experimental assessment of new lighting strategies and monitoring tools, managers and conservators of archaeological sites characterised by high humidity and the development of phototrophic biofilms will profit of these results. The methodologies developed in the frame of this study have the additional advantage that can be adapted to apply to any other archaeological or historical site at which biological decay of rock surfaces is occurring. Up to date, the circulation of papers within the scientific community and the participation at national and international meetings substantially contributed to exploitation of major results, while the illustration of these methodologies in undergraduate and postgraduate courses in restoration, environmental and biological sciences is improving knowledge and understanding of the problems connected to a safe management and conservation of archaeological sites.

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European project details

CATS, EVK4-CT2000-00028, Cyanobacteria Attack Rocks: control and preventive strategies to avoid damage caused by cyanobacteria and associated micro-organisms in Roman hypogean monuments, Co-ordinator: Patrizia Albertano.

The BIOBRUSH Project– Scientific Research on Bioremediation and its Potential for Conservation Practice on Stone Monuments

Contract No. EVK4-CT-2001-00055

Project Coordinating Institution
University of Portsmouth
School of Biological Sciences
King Henry Building
King Henry 1 Street
Portsmouth PO1 2DY
United Kingdom
Project Administrator: Dr Alison Webster

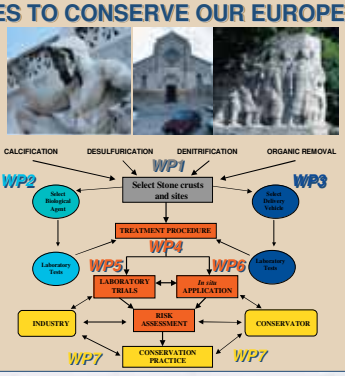
BIOBRUSH Scientific Contractors
Dr Eric May, University of Portsmouth (Coordinator)
Dr Jan Kuever, Stiftung Institut fur Werkstofftechnik, Bremen, Germany
Prof Claudia Sorlini, Universita Degli Studi di Milano, Italy
Dr Linda Krage, Riga Technical University, Latvia
Prof Andreas Vgenopoulos, National Technical University of Athens, Greece
Dr Emilio Mello, Syremont S.p.A, Pescara, Italy

Subcontractors
Prof Giancarlo Ranalli,
DISTAAM, Universita del Molise, Italy
Dr Thomas Warscheid,
Ibw-bioconsult, Oldenburg, Germany
Dr Franz Moll,
ars restauro, Bremen, Germany

Researchers
Dr Robert Inkpen, University of Portsmouth
Dr Dimitrios Katsinis, National Technical University of Athens
Dr Francesca Cappitelli, Universita Degli Studi di Milano
Dr Elisabetta Zanardini, Universita Degli Studi di Milano
Curt Rudolph, Stiftung Institut fur Werkstofftechnik
Dania Zamarreño, University of Portsmouth
Inese Sidraba, Riga Technical University

BIOBRUSH: BIOremediation for building Restoration of the Urban Stone Heritage
NOVEL APPROACHES TO CONSERVE OUR EUROPEAN HERITAGE

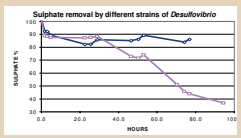
The formation of detrimental **crusts** on stone is a very real **problem** in European cities. Industrialisation in the last century has led to alterations caused by inorganic **atmospheric pollutants** such as **nitrogen** oxides and **sulphur** dioxide produced by the combustion of petroleum and its derivatives. The compounds are oxidized in the air into nitric and sulphuric acid, respectively, that, after deposition on the surface of stone carbonates, are converted into **sulphates** and highly soluble **nitrates** which are easily washed away by rain. Atmospheric particulates also mix with **gypsum** crystals produced by sulphuric acid leading to the creation of disfiguring **black crusts**.

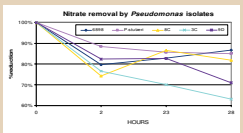


The novel approach of the BIOBRUSH project was to use different bacteria to **mineralise** stone salts in crusts and **consolidate** using biocalcification. The technology links the two processes and applies bacteria and their nutrients to stone surfaces using **delivery systems** that are safe and environment-friendly. The bioremediation approach **supplements** existing conservation technologies, which can often be ineffective or toxic to end-users or the environment. **BIOBRUSH** research has **established the risks** to heritage stone and the limitations of bioremediation in **conservation practice.**

Salt Crust Removal: Sulphate-reducing Bacteria

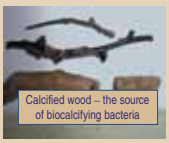
Strains of bacteria able to degrade polyaromatic hydrocarbons (PAH), nitrate reducing bacteria and sulphate reducing bacteria (SRBs), have been selected from existing culture collections. The selected bacteria were then compared for their ability to degrade PAH and reduce nitrate and sulphate respectively. Assessment of nitrate and sulphate removal was made by ion chromatography analysis





Stone Consolidation: Biocalcifying Bacteria

Bacteria from a freshwater stream in England were isolated and tested for their ability to produce calcite. Calcite production in culture is seen within 24 hours under the light microscope (x 40) and on stone by SEM (x 4,000).

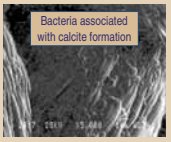

Calcified wood – the source of biocalcifying bacteria


Bacterial growth on laboratory media


Calcite crystals embedded in growth


Bacteria embedded within calcite crystals


Crystals isolated from growth


Bacteria associated with calcite formation


Calcite deposition on limestone by bacteria

Performance Assessment: Laboratory and Field Trials

The stone was tested in the laboratory, prior to field trials. Sample properties, including mineralogy and bulk physical properties, were assessed. This evaluated RISKS to minerals and stone integrity and EFFICIENCY of salt removal and consolidation with biocalcite.


Performance was assessed in field trials using an agreed experimental matrix


Stone thin sections treated with carbogel delivery system containing bacteria


When possible, stone (here Duomo, Milan) was tested *ex-situ* to assess crust removal


Building trials were done with the cooperation of local conservators


Stone sections were examined by light microscopy to assess any adverse effects


Stone blocks were treated with delivery systems to evaluate performance


Treated areas were assessed visually and chemically immediately and after 6 months

Database of Microorganisms

Isolation from environment and selection from culture collection
Assessment of capabilities: sulphate reduction,nitrate reduction, calcite production
Determination of Hazard Category

Database of Stone Artefacts

Categorisation of stone. Details of weathering and crust formations.
Analysis of crust composition: sulphate, nitrate and chloride ions
Details of local conditions

Involvement and Information for End-users

BIOBRUSH trials throughout were done in cooperation with conservators. The databases generated by the BIOBRUSH project will provide information for those working with Cultural Heritage throughout Europe. These databases will be updated. Culture collections held by partners are linked to these databases.

e-mail: BIOBRUSH@port.ac.uk **www.BIOBRUSH.org**

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BIOBRUSH – scientific research on bioremediation and its potential for conservation practice on stone monuments

Eric May

Coordinator, on behalf of the BIOBRUSH consortium, School of Biological Sciences, University of Portsmouth, UK

Key words: bioremediation, black crusts, salt removal

Introduction and content

The occurrence of salt crusts and incrustations on stonework in monuments, caused by nitrate and sulphate pollution, induces accelerated weakening and deterioration of the matrix. Until now, the remediation of stone pathologies such as black crusts, containing sulphate and uncombusted hydrocarbons, has been carried out using chemical or physical methods, often associated with detrimental effects. Even when water is used, as for nitrate removal, it can permeate the stone and cause negative effects. There is considerable evidence that microorganisms can remove salts that accumulate in crusts of damaged stone [1, 2] while others have been shown to deposit minerals that consolidate stone materials [3, 4]. The EC-funded project BIOBRUSH aimed to produce an innovative treatment based on bioremediation, combining *crust destruction* (by mineralising bacteria) with *mineral production* (via biocalcification). The BIOBRUSH research objectives were:

1. To assess stone crusts from historic buildings and monuments across Europe
2. To establish a European bacterial culture collection for use in stone bioremediation
3. To investigate the efficacy and optimise the stone bioremediation process
4. To carry out risk assessments on stone minerals and bulk properties in laboratory studies
5. To perform *in situ* field trials on buildings or monuments

BIOBRUSH generated two databases of information: one concerning the nature and extent of crusts on buildings in Northern and Southern Europe, the other detailing microorganisms with bioremediation potential for conservation work. Stone Sample Information Sheets compiled site and stone characteristics from 13 monuments, mainly in Latvia, Greece and Italy, covering 22 natural stones with evidence of salt deposits and incrustations, that were subjected to mineralogical, chemical and biological analyses. The nature of crusts in European buildings was found to be very varied. Physical properties of crusts showed remarkable shifts towards greater porosity within the weathered uppermost layers of the rocks and plaster, which are ideal for bioremedial techniques. Sulphates were often present in a narrow 40 mm surface zone of stone blocks. High levels of sulphate were detected in stone from Matera Cathedral, Riga Brethrens cemetery, Lübeck townhall and Melos. Sulphate concentrations at Matera were found to be much more variable than nitrate. Nitrates, which could only be detected at Matera Cathedral and Riga Brethrens cemetery, formed a much more limited gradient in the surface zones. Generally, salt concentrations showed great variability, which may cause major difficulties in bioremediation treatments. Organic pollutants were found at very low levels, unsuitable for bioremediation using organic-degrading bacteria. BIOBRUSH assembled a culture collection of bacteria with organic-degrading, sulphate-reducing, nitrate-reducing and biocalcifying activities. The potential of bacteria to remove crusts was assessed in laboratory experiments and candidate organisms identified. Risk assessments were done to reduce possible detrimental human health

effects and adverse reactions on cultural objects. Field trials at a wide range of locations in Europe were completed in Greece, Latvia and Italy. Considerable variations were observed in the performance of SRB and NRB during laboratory and field trials. In many cases the effect of the carrier system masked any effects by the bacteria. The data indicate that success with SRB was greater with low porosity stones while NRB were more likely to work with stones of higher porosity, although the latter also worked with marble. On the basis of the results obtained with this project it is possible to consider biotreatment using viable cells as a very good tool for sulphate and nitrate removal in certain cases. The negative impact of this application was small. The use of enzymes instead of viable cells was not possible due to lack of availability on the market. The traditional methods based on mechanical, physical or chemical tools are often not satisfactory enough; in fact, some of them create risk for the stone, while others do not solve the problems because nitrates are highly soluble. For this reason biological methods investigated in the BIOBRUSH programme may be preferable and, with appropriate application procedures, can be reliable [5]. The time for biological application is comparable to that for traditional methods. BIOBRUSH explored the limitations of bioremediation for the conservation of stone and recommended practical outcomes to allow use by restorers alongside other traditional methods.

European dimension

Deterioration of cultural heritage is a severe problem in European cities and urbanised developments. The relevance of this problem therefore reaches across all Europe. To investigate the elimination of pollution and salt stress from stones, an interdisciplinary approach from different scientific fields was applied Europe-wide. In essence this meant an international exchange of know-how to understand underlying deterioration processes and ideas to develop treatment strategies for stonework affected by adverse salt environments. The study of a wide range of different objects exposed to different climatic conditions with different levels and qualities of environmental pollution in a European-wide approach has led to the accumulation of significant results concerning the use and limitations of bioremediation in Europe. *Stone Information Data Sheets* were catalogued in BIOBRUSH to create an extensive database of information about stones showing crust and salt accumulation in buildings of cultural heritage in different climatic zones of Europe. Microbial agents suitable for use in bioremediation of weathered artistic stoneworks were assembled, selected appropriately from those classified as safe on the basis of current European regulations. These microbes constitute a culture collection that is available to European workers. Information on these organisms and others studied was compiled in a database of *Microorganism Data Sheets* that provides background information on strains in the culture collection.

Innovation and originality

The novel basic aim of the BIOBRUSH project was to sequentially link the mineralisation processes of desulfurication, denitrification and organic removal to the consolidation phenomenon of biocalcification, investigate different heritage materials under different climatic situations and integrate the findings into conservation practice. The ultimate goal was to provide an effective, environmental-friendly biotechnological tool for restoration and conservation of artistic stoneworks. The biological methods explored in BIOBRUSH were less harsh than the chemical and physical ones, which are often destructive methods. Removal of altered surface material by microorganisms takes place in a natural way since they play an active role in the environment where they contribute to closure of some biogeochemical cycles. The substitution of biological techniques for potentially toxic chemical and harsh physical methods is thus in line with EU policy.

Impacts

BIOBRUSH was driven by the need for a systematic investigation and rigorous experimental testing, building on existing research and focusing on practical outcomes, to inform end-users about how such bioremediation procedures could be used in conservation. It was a central aim of this project to bring together the people who will be able to educate, inform and influence opinion among user-groups. Four of the partners were Universities and involved in education of future generations of scientists, conservators and industrialists; two were directly concerned with the education of conservators and therefore have a direct influence on the attitude of the conservation community to the new possibilities offered by technology based on bioremediation. Two members of the consortium were industrial partners that are directly concerned with solving conservation problems across a wide front. Their involvement ensured that practical issues were always to the fore and that BIOBRUSH outcomes will be made known to practitioners. At the beginning of the research programme the consortium adopted a deliberate research strategy that required every partner to select appropriate stone heritage materials from historic sites under repair or at which restoration was planned. We needed to identify original damaged stonework that was available in sufficient quantity for future treatment applications. We therefore had to contact and consult with restorers and local superintendents who could indicate possible sites to the consortium suitable for our work. Field trials in the last phase of BIOBRUSH were originally restricted to Latvia and Greece, but these were extended to Italy and this has necessarily involved more consultation with conservators. The activities of the BIOBRUSH project and the engagement of conservators in the research has provided a basis for informing conservators at a management level about the use of bioremediation and this will cascade down to other personnel specialized in the protection and conservation of stone monuments.

Acknowledgements

Funds from the EC under 5FP; support from Michel Chapuis; project facilitation from Dr Alison Webster; scientific management from Dr Thomas Warscheid & Dr Jan Kuever (Bremen), Prof. Claudia Sorlini (Milan), Dr Linda Krage (Riga), Prof. Andreas Vgenopoulos & Dr Dimitrios Katsinis (Athens), Dr Emilio Mello (Syremont); practical expertise from Dr Rob Inkpen, Dr Giancarlo Ranalli, Dr Francesca Cappitelli, Dr Elisabetta Zanardini, Curt Rudolph, Dania Zamarreño, Inese Sidraba, Franz Möll.

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European project details

BIOBRUSH, EVK4-CT-2001-00055, Bioremediation for Building Restoration of the Urban Stone Heritage in European States, *Coordinator* Dr Eric May, University of Portsmouth.

THE BIOPROTECTION PROJECT ON THE "MADARA HORSEMAN" (BULGARIA) – BIOREMEDIAL TECHNIQUES IN THE CONSERVATION OF STONE MONUMENTS

Th. Warscheid[1], G. Orial[2], E. v. Plehwe-Leisen[3] and V. Tudorov[4]

[1] LBW - Bioconsult, Wiefelstede, Germany
[2] L.M.R.H.- Laboratoire de Recherche des Monuments Historiques, Champs s/M, France
[3] Untersuchungslabor für Fragen der Natursteinerhaltung (LPL), Cologne, Germany
[4] National Academy of Fine Arts Dept. Conservation, Sofia, Bulgaria

Key words: Madara Horseman, biodeterioration, bioremedial techniques, conservation, calcitic stone

Introduction

The Madara Horseman (MH) is a relief, sculptured in the very beginning of the 8th century situated on the western vertical surface of a rock massif facing the Madara plain, in north-eastern Bulgaria. The Madara Horseman is a symbol of national pride and self-determination for Bulgaria. It is Europe´s only relief of a horseman carved in a live rock massif, but this enduring signature of Bulgarian culture flakes away with every season (Fig. 1).

Besides massive static problems due to the geological nature of the rock massif and percolating humic water from the vegetation on top of the hill, the relief of the "Rider of Madara" is obviously endangered by the microbial infestation of lichens, algal and fungal growth causing a massive bio-corrosive attack as well as biofouling modifications to the calcitic rock (Fig. 2).

Fig. 1: Relief of the "Madra Horseman" with wetting areas caused by rainfall and perculating humic water streams.

Fig. 2: Detail of the relief showing heavy erosion and flaking of the rock surface leading to loss of historical substance.

Fig. 3: Detaching rock shales as consequence of microbial boicorrosion and biofouling of the calcitic rock at Madara.

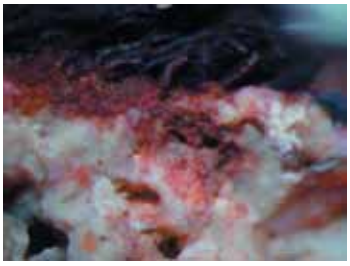

Fig. 4: Microbial biofilm, red coloured by PAS- staining, penetrating up to one cm into the calcitic rock

Objectives of the project

In order to develop an effective and long-term sustainable conservation strategy of this unique rock monument, the "Madara"- bioprotection project consists of
(1) an entire microbiological anamnesis and evaluation of the microbial impacts
(2) a long-term testing of biocidal resp. cleaning treatments in context with the microbial removal of gypsum residues by sulphate-reducing bacteria and biocon-solidation by calcite-forming bacteria
(3) materialspecific analysis (capillary water uptake, drilling resistance and thin-slide sections) of the rock at site to prove the efficacy and consequences of the above mentioned bioremedial treatments
(4) the integration of furtherleading conservation treatments (consolidation, fixation of rock shales, regulating water perculation) referring the further damage factors at site.

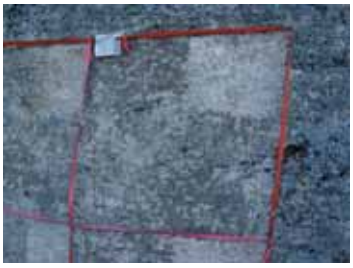

Fig. 5: Result of biocidal treatment and partly mechanical cleaning on the test field area six month after application

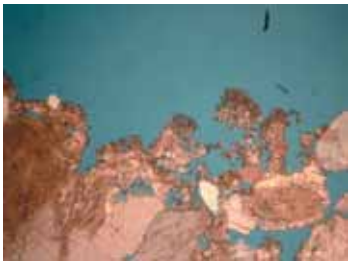

Fig. 6: After biocidal treatment and mechanical cleaning the pore system is opened for the biocalcifying application

Preliminary results of the project

At the actual stage of this research project, it can be stated that during the microscopical, microbiological and material-specific investigations an important microbial induced impact in the degradation of the calcitic rock at the relief of Madara Horseman could be proven (Fig. 3):
- The rock profile showed a high content of moisture due to microbial biofilms blocking the pore system and limiting the dessication of the constantly wetted rock.
- Microscopical analysis demonstrated that the microorganisms penetrate up to one cm into the rock (Fig. 4).
- Measurements of drilling resistance confirmed their biodeteriorating activity indicated by a weak rock zone up to 2 - 3 cm under-neath the lichens thalli until the original strength has been reached.
- Effective biocidal treatments could be achieved in order to remove lichens (Fig. 5).
- Biocalifying bacteria showed attraction to consolidate porous calcitic rock (Fig. 6).

European dimension

The studies for conservation of the relief of Madara Horseman were realized following the recommendations of an UNESCO-Roundtable dated 18th - 22nd June 2003. The interdisciplinary cooperation of scientific institutes in Bulgaria and France as well as applied SME-partners in Germany was substantial stimulated by the european "BIOBRUSH"-project („Scientific research and practical transfer of bioremedial techniques in the conservation of stone monuments", Contract-No. EVK 4-CT-2001-00055, 2002-2005) following the bioremedial approach in the practice of stone conservation.

Acknowledgement

The project consortium wishes to thank
- National Council for Monuments within the Ministery of Culture of Bulgaria as well as
- Globul (Cosmo Bulgaria Mobile EAD)

for the financial support to initiate and proceed within the ongoing research project.

Future perspectives

The formation of detrimental crusts caused by the enrichment of salts and biopatina is a very real problem in the conservation of cultural heritage in Europe originating from the coincidence of sustained economic growth and industrialisation. Addressing those problems, the application of bioremedial techniques may serve as an important practical tool to meet referring conservation strategies, the project consortium intents a furtherleading research proposal on the risks, benefits and limitations of those biotechniques for natural historical sites within the 7th EU frame programme

The bioprotection project on the "Madara Horseman" (Bulgaria) – bioremedial techniques in the conservation of stone monuments

Th. Warscheid[1], G. Orial[2], E. von Plehwe-Leisen[3] and V. Tudorov[4]

[1] LBW – Bioconsult, Wiefelstede, Germany
[2] L.M.R.H. – Laboratoire de Recherche des Monuments Historiques, Champs s/M, France
[3] Untersuchungslabor für Fragen der Natursteinerhaltung (LPL), Cologne, Germany
[4] National Academy of Fine Arts Dept. Conservation, Sofia, Bulgaria

Key words: Madara Horseman, biodeterioration, bioremedial techniques, conservation, calcitic stone

Introduction and content

The Madara Horseman (MH) is a relief (measuring 6 × 4 m), sculptured in the very beginning of the 8th century situated on the western vertical surface of a rocks massif facing the Madara plain, in north-eastern Bulgaria. The Madara Horseman is a symbol of national pride and self-determination for Bulgaria. It is Europés only relief of a horseman carved in a live rock massif, but this enduring signature of Bulgarian culture flakes away with every season (Fig. 1). Besides massive static problems due to the geological nature of the rock massif and percolating humic water from the vegetation on top of the hill, the relief of the "Rider of Madara" is obviously endangered by the microbial infestation of lichens, algal and fungal growth causing biocorrosion (i.e. acid attack and transfer of calcite binder by carbonic and organic acids, oxalate precipitation) as well as biofouling (i.e. thermal-hygric impacts of biofilm, deliberation due to swelling and shrinking of mucuos biofilm, deposition and accumulation of airborne particles leading to crust formation, changes in capillary water uptake and moisture retention) processes within the uppermost layers of the respective calcitic rock (Fig. 2) [1].

Figure 1: The relief of the Madara Horseman above the sightseeing construction; left hand scarfolding for the project activities

Figure 2: Detaching rock shales as consequence of microbial biocorrosion and biofouling of the calcitic rock at Madara

Due to the widespread corrosion and scaling of the calcitic rock, it is the aim of the research project presented here to develop an effective and long-term sustainable conservation strategy of this unique rock monument based (1) on an entire microbiological anamnesis and evaluation of the microbial impact in the rock deterioration at Madara, (2) a long-term testing of possible biocidal and cleaning treatments (Fig. 3a,b) and the application of microbial desalination and consolidating biocalcification following (3) materialspecific analysis (i.e. capillary water-uptake, drilling resistance and thin-slide sections) of the rock at site before, during and after the

above mentioned treatments (Fig. 4a,b) as well as (4) the integration of further conservation treatments (i.e. fixation of scales, regulating water percolation, consolidation) referring the further damage factors at site, such as static problems and percolating humic waters [2].

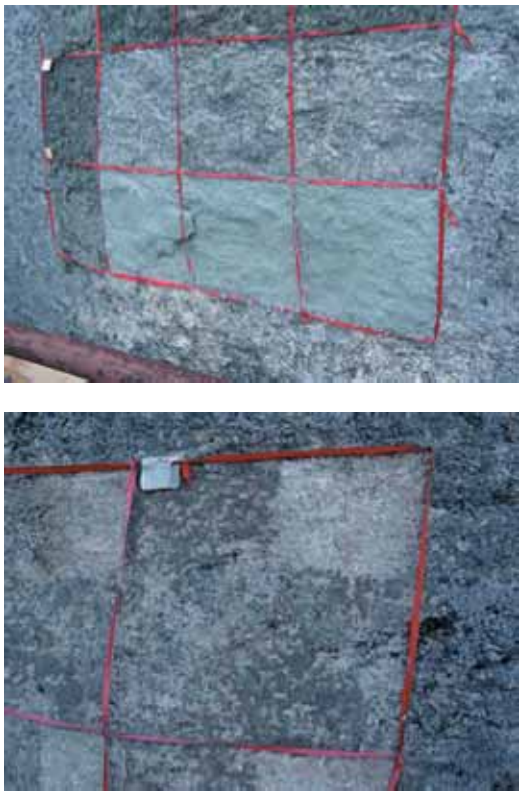

Figure 3: Biocidal treatment. a) biocide test field with cellulose- and clay-containing compresses besides liquid applications, b) six month after biocidal treatment and partly mechanical cleaning (right above)

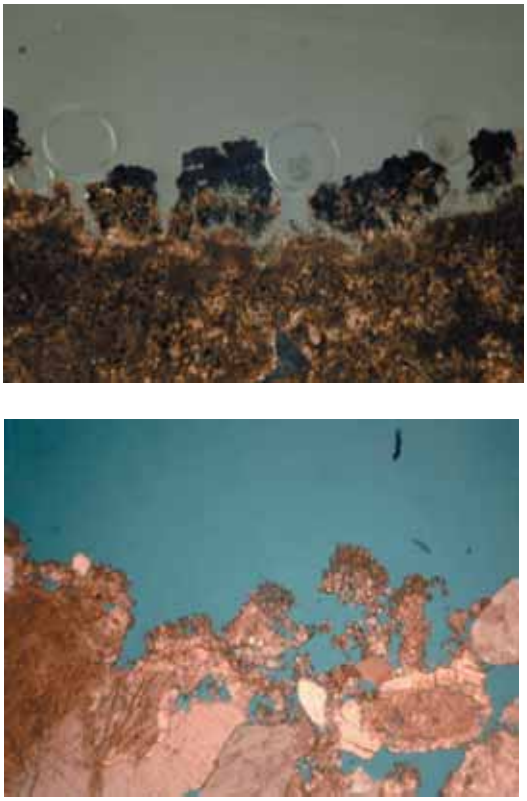

Figure 4: Thin slide section analysis. a) untreated areas show the lichens infestation within the rock profile, b) after the biocidal cleaning the entire removal of the microbial biofilm can be achieved

At the actual stage of this research project, it can be stated that during the past microscopical and microbiological investigations the important impact of lichens and accompanying microorganisms in the degradation of the calcitic rock at the relief of Madara Horseman due to biocorrosion and biofouling could be proven. Materialspecific measurements revealed that the rock profile at site shows a high moisture content in lichens contaminated areas and less humidity within noninfested areas. The capillary water uptake of rock is mainly reduced in lichens infested areas, giving hint that the pore system in this areas is significantly blocked due to microbial biofilms, hindering thus an effective dessication of the constantly wetted rock. The analysis of thin-slide-sections show that microorganisms are penetrating up to one cm into the rock and their biodeteriorating activity seems to be confirmed by the measurements of drilling resistance indicating an outer crumbling zone of similar extent, followed by a weak, because wet, rock zone up to 2-3 cm until the original strength has been reached again. In conclusion, the lichens infestation at the relief of the Madara Horseman needs to be removed and long-term controlled by a most effective biocidal and cleaning treatment achieved within the referring testfield operations Following the removal of lichens, the crumbled surface of rock will be partly desalinated from gypsum residues using sulphate-reducing bacteria and finally consolidated by calcite-forming bacteria [3]. The efficacy of those treatments and later consequences for the rock material will be evaluated during materialspecific investigations.

European dimension

The studies for conservation of the relief of Madara Horseman described here, are realized following the recommendations of an UNESCO-Roundtable dated 18th-22nd June 2003 and represents a unique interdisciplinary cooperation of scientific institutes in Bulgaria and France as well as practice-orientated SME-partners in Germany favouring the application of modern analytical tools and bioremedial techniques in the conservation of stone monuments with special emphasis to further european conservation activities in regard to education or practical application in the new up-coming, easteuropean member states in the EU.

Innovation and originality

The technical tools of the microbiological anamnesis, the materialspecific analysis and bioremedial applications are mainly based on the scientific progress and noval developments achieved during research activities within the European community during the last fifteen years. Especially the recent european funded "BIOBRUSH"-project ("Scientific research and practical transfer of bioremedial techniques in the conservation of stone monuments", Contract-No. EVK 4-CT-2001-00055, 2002-2005) gave substantial support and stimulation to follow the bioremedial approach in the conservation practice within the project presented here.

Impacts

The formation of detrimental crusts caused by the enrichment of salts and biopatina is a very real problem in the conservation of cultural heritage in Europe originating from the coincidence of sustained economic growth and industrialisation with the location of an important part of the world's cultural inheritance. Thus, it is only through an European initiative that rapid action can be brought to-bear on this serious problem by a careful invention of bioremedial measures across the EU. The project presented here shows a first attempt how the transfer of bioremedial techniques into the conservation practice can be achieved via the cooperation with referring SME, addressing more closely their risks, benefits and limitations for heritage objects (i.e. aesthetic consequences, reversibility, durability), the environment and end-users (i.e. health problems, aerosols) in order to seek opinion and ensure that the research outcomes influence conservation policies and practice.

Acknowledgement

The authors and project members wish to thank the National Council for Monuments within the Ministery of Culture of Bulgaria as well as Globul (Cosmo Bulgaria Mobile EAD) who financially supported the initiation and recent proceeding of the ongoing research project.

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European project details

In order to continue the project activities more profoundly in regard to the development general conservation strategies for natural historical sites, the members of the consortium is going to prepare a referring research proposal within the upcoming 7th EU frame programme.

FLUOROSILICATES ("FLUATS") USED IN THE PAST IN THE CONSERVATION OF STONE IN CENTRAL EUROPE

Ivana Kopecká[1], Vratislav Nejedlý[2], Lubomír Kopecký[3], Jiří Novotný[4]

[1] National Institute for Cultural Heritage, Central Institute in Prague. Czech Republic

[2] National Institute for Cultural Heritage, Central Institute in Prague. Czech Republic

[3] Czech Technical University in Prague, Faculty of Civil Engineering. Czech Republic

[4] University of Pardubice, Faculty of Restoration. Czech Republic

In Central Europe stone sculptures were made almost from porous stone like sandstone. Relatively high porosity of the stone and strong continental climate north of the Alps caused intensive degradation of the stone surface. In Bohemia and Moravia oil varnishes were used traditionally as protection of the surface of stone. About 1850 the view of art historian of the artistic qualities of stone sculptures changed. In consequence requirements on artistic quality of the stone restoration changed too. Only pure raw stone surface was tolerated. Respecting these requirements was facilitated by using new materials for the consolidation of degraded stone surfaces. First soluble glass was used as stone consolidant. After its application some damage on the stone surface was found. This fact started using fluorosilicates (fluats) for stone consolidation and fluats were recommended by cultural heritage authorities as proved consolidants for stone sculptures. A lot of damage to stone sculptures is put down to this kind of conservation, but until now using fluorosilicates has never been confirmed exactly by chemical analysis

At the beginning of the 20th century fluats were used in a similar way for the restoration of many stone sculptures in Bohemia and Moravia. For example, in 1923 then sandstone statues on the Charles Bridge and the Royal Summer House in the Royal Garden of Prague Castle (Belvedere) built of sandstone and decorated with splendid, very fine stone relief.

1

2

3

1- Royal Summer House in the Royal Garden of Prague Castle

2, 3 – stone decorations of Belvedere in exterior

4 – well preserved stone decoration inside the loggia

4

During the recent research work carried out on the building of Belvedere, degradation of stone different in intensity and type, has been observed, especially after cleaning. Perfectly conserved large areas have also been found. Evidently paler areas can be seen there – smoother sintered fluated surface - and distinctive dark areas – from which the fluated layer has broken away (probably due to pressure of crystallization). In the latter areas the stone is stripped and opened and its specific surface, in comparison with fluated surface, is huge. This fact and high air pollution result in faster degradation of stone in these areas. On the facade of Belvedere these damaged areas are clearly situated in those parts of the building where rain and salts (evolved from ancient cement restorations) penetrate into the construction.

5

6

5, 6, 7, 8 - different types of degradation on the surface of stone in details

7

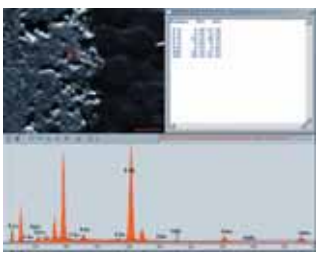
8

The process of stone consolidation using hexafluorosilicates can be described in the following:

1. corrosion of grains of quartz on the surface of stone
2. sintering of the layer on the top layer of stone

This layer is very thin, homogenous, nonporous with the character of glass. Its thickness was established by analysis under 10 microns. The areas of stone surface without content of moisture and water soluble salts can be very well protected by this layer (against sudden changes of climate, against abrasion, air pollution,…). On the contrary, if this nonporous glass layer is covering stone with the content of moisture and water soluble salts, crystallization of salts and freezing of water below this layer causes breaking away of areas of this layer from the stone.

Last year several samples of stone surface were analysed (as cross sections) by the scanning electron microscope XL 30 ESEM-TMP PHILLIPS equipped with the EDAX® multichannel X-ray spectrometer for elementary microanalysis. Fluorine was detected in a very thin layer on the treated surface of stone. The morphology of this layer is completely different from that of non-treated stone.



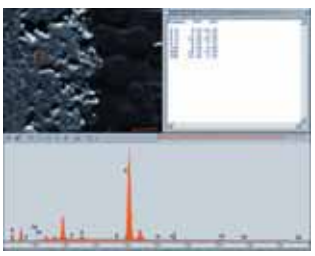


Fig. 9 and 10 - SEM photos of cross-sections of stone and spectrum of EDS X-ray analysis (Si and Al are excluded from quantitative analyses because of stricter delimitation of the fluated layer). Area in the red frame was analysed.

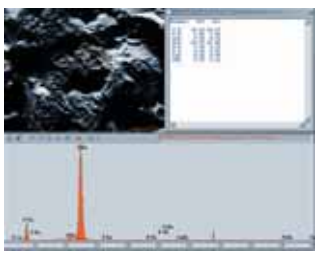


Fig. 11 - SEM photo and X-ray analysis of the sintered surface of stone

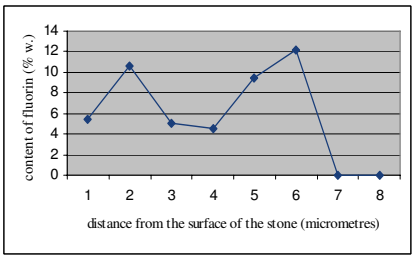


Fig. 12 - Relative content of fluorine in accesory elements in the top layer of stone depending on the distance from the surface

Backward evaluation of the use of fluats is mostly critical because a lot of stone work was damaged after this treatment (mainly the stone used in construction, especially pedestals, the parts of buildings often saturated by moisture and by water soluble salts). On the other hand, it is just to say that a lot of stone sculptures - including the excellent filigran stone decoration of the Belvedere building were partly conserved or saved due to its consolidation by means of fluats at the beginning of the 20th century…