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Proceedings
of the 7th European Conference "SAUVEUR"

SAFEGUARDED CULTURAL HERITAGE

Understanding & Viability for the Enlarged Europe

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Volume 1 – Papers

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Editorial Note

International scientific projects in the field of cultural heritage have received European funding for more than twenty years. Though the financial support may not always have been as high as we would have liked, major results have been achieved with the help of researchers from many countries and a combination of national and European programmes.

The European Conferences on cultural heritage research have become regular milestones on the never-ending journey of discovery in the search for new knowledge. They also provide opportunities to make a brief review of the results, and to draw new inspiration. The programme prepared for this conference included 83 oral presentations and 134 poster and demonstration stands, reflecting the rich background and wide scope of our work. Nearly 300 delegates from 37 countries in the world attended the conference, which supported free participation of students presenting the outcomes of their research work.

This Conference was held just before the final negotiations in the European Parliament and the Council on the 7th Framework Programme of the European Community for research, technological development and demonstration activities in the next seven years. The programme therefore included themes aimed at enhancing and strengthening our common endeavour to create necessary and efficient conditions for future research on issues of cultural heritage.

The Conference sessions clearly showed the complexity of research into cultural heritage, where strong, well-planned collaboration among the natural, technical, economic and social sciences is needed in order to achieve reasonable and fruitful results. Nevertheless, our experience shows that a narrow approach dealing with a single task usually creates difficult problems that can lead to severe losses in the cultural heritage, or can damage our quality of life. Lack of support for interdisciplinary projects is a major deficiency of all grant systems and schemes. Bearing this in mind, we should support all ways of incorporating cultural heritage themes into as many priorities and calls of 7th Framework programme as possible.

An interdisciplinary approach should also be reflected in our cooperation with business and industry, namely with the wide range of small and medium-size enterprises working in the field of cultural heritage.

Safeguarding the cultural heritage is frequently interpreted as change management. Joint European research produces a scientific background and support for such management. We are living in a period characterised by rapid and remarkable changes in the environment in a general sense. Natural change and man-made changes, including climate change, as well as societal change, form an ever-changing and colourful stage not only for our research but also for the management of society. Close cooperation with policy makers is therefore a significant feature of cultural heritage research.

Cultural heritage issues and problems are essential elements of our everyday life, namely in relation to quality of life, social and economic welfare and stability. Therefore, it is very important that a wide public is involved in management of the cultural heritage, and it is very useful to inform European citizens about recent scientific achievements. For the first time in the history of these conferences, the 7th European Conference in Prague opened its poster exhibition and demonstration saloon to a public audience, a further step in opening up European science to the public.
A special session was devoted to cooperation in educational programmes and national research programmes. The need to promote the establishment of a network coordinating such cooperation was apparent, and this session was well supported. The same is true for cooperation

between research and industry, where an important development was the creation of the European Construction Technology Platform with a special targeted activity – the Cultural Heritage Focus Area. This has national parallels establishing national research agendas.

The final session invited selected representatives of international bodies and organizations, who presented persuasive contributions illustrating that European research into cultural heritage has a high international value beyond the borders of the European Union.

The papers presented during the conference sessions are gathered in the first volume of the proceedings, while the posters, accompanied with an extended summary, are published in the second volume. The two volumes thus provide rich material for study, inspiration and dissemination of knowledge.

The editors wish to thank everyone who contributed with deep enthusiasm and involvement to the organization of the conference, to the presentations, and to these proceedings for their valuable co-operation, without which the event could not have been successful.

SUMMARY

The 7th European conference on the Cultural Heritage: "Safeguard Cultural Heritage-Understanding Understanding & Viability for the Enlarged Europe"

The 7th European conference on Cultural Heritage research was held in Prague from 31st May – 3rd June 2006. The conference was supported under the 6th Research Framework Programme (Specific Support to Policy). It was organised in cooperation with the European Commission by the Institute of Theoretical and Applied Mechanics (ITAM) of the Academy of Sciences of the Czech Republic following the earlier conferences in Rome (1997), Aachen (1998), Santiago di Compostela (1999), Strasbourg (2000), Cracow (2002) and London (2004).
The overall aim of the conference was the consolidation and impact assessment of results achieved in EU research projects related to the movable, immovable and infrastructure applied to cultural heritage with a special focus on exploitation and spin-offs of cultural heritage research results and testing the acceptability of new technologies and sustainability approaches by the user community, SMEs, owners, managers, conservationists and restorers of the cultural heritage.

Its specific objectives were in particular to:

- Highlight the role of European cultural heritage research within international activities and co-operation.
- Assess the impact of EU policies on the conservation of European cultural heritage and evaluate the positive contribution of cultural heritage research for competitiveness and job creation.

- Disseminate the results of EU cultural heritage research acquired at large research facilities and discuss new development and innovations in research infrastructure.
- Discuss and consolidate co-ordination of national research and educational programmes for cultural heritage within the enlarged Europe.
- Refine ideas and visions of the European Technology Platforms opened to cultural heritage issues in the context of preparation of the 7^{th} Framework Programme.

More than 280 participants from 37 countries representing a large number of research and end-user organisations from the public and private sector took part in 210 oral presentations and posters covering the plenary sessions on “The impact of EU policies on European cultural heritage”, “Coordination of national research and education”, and “Challenges of European cultural heritage” as well as the parallel sessions on the “movable heritage”, the “immovable heritage”, “Cities, landscapes and villages”, and “Research infrastructure” applied to Cultural heritage. The poster exhibition gathered almost 100 posters related to the themes of the parallel sessions, and a "demonstration salon" was opened to innovative products and processes.

During the conference, attention was especially driven on the fact that there is a wide range of accumulated problems in historic settlements affecting the movable and immovable heritage and related to environmental changes, social impacts, economic issues, growing tourism and inadequate cultural heritage management as well as threats from natural hazards. All these issues require that cultural heritage research continues to develop advanced environmental technologies through the knowledge generated from basic research and the adaptation of scientific developments from other sectors. All stakeholders expressed a strong demand that the cultural heritage be mainstreamed into EU and national policies and research programmes.

In the final plenary session in the ceremonial Spanish Hall of Prague Castle, the Conference adopted the Prague concluding Message. This document presents the joint standpoint of representatives of major European and international bodies supporting cultural heritage research including the European Commission, UNESCO, Council of Europe, ICOMOS, ICCROM, ICOM, Europa Nostra, Organisation of World Heritage Cities, Getty Conservation Institute..; to summarise these conclusions, all stakeholders expressed a strong demand that the cultural heritage be mainstreamed into EU and national policies and research programmes. In this respect, the European Institutions should support the incorporation of cultural heritage themes into relevant priorities and tasks of 7^{th} Framework programme, and mitigate unintentional negative effects on cultural heritage of other EU legislation in application of the article 151.4 of the EC Treaty; in addition, the value of cultural heritage research revised should be explicitly mentioned in the revised EU Sustainability Strategy, and the newly established European Research Council (ERC) should consider in its programmes the importance of basic research for cultural heritage.

Beyond the EU, National and Regional Governments and relevant authorities in Europe should integrate in their research programmes scope for cultural heritage research and support for related research infrastructure, and facilitate ways of overcoming the fragmentation of research for the cultural heritage research community. Finally,, public-private partnerships as specific European Technology Platforms (e.g. construction, chemistry) are expected to take into account the specific needs of cultural heritage in order to respond to new and complex challenges as mentioned above, and non governmental organizations should promote further public participation in cultural heritage research which favourably impacts on the environment, energy, sustainability and quality of life.

CONFERENCE SCIENTIFIC PROGRAMME

May 31, 2006 **Venue: Panorama Hall, Prague Congress Centre**

Opening Session
Chairperson: Miloš Drdácký (Czech Republic)

1	15.00-15.10	Václav Pačes	President of the Czech Academy of Sciences
2	15.10 -15.20	Alena Štěrbová	Vice-minister for European Integration and International Affairs, Ministry of Education, Youth and Sports, Czech Republic
3	15.20-15.30	Kateřina Kalistová	Vice-minister, Ministry of Culture, Czech Republic
4	15.30-15.40	Jan Slanina	Vice-minister, Ministry for Regional Development, Czech Republic
5	15.40-15.50	Michel Chapuis	European Commission, Directorate General 'Research'
6	15.50-16.00	Josef Štulc	President of ICOMOS Czech National Committee

Overview of poster presentations

7	16.00-16.30	Matija Strlič (SI)	Movable heritage
8	16.30-17.00	Cristina Sabbioni (IT)	Immovable heritage
9	17.00-17.30	Jacques Teller (BE)	Cities, villages and landscapes

Official opening of the Poster Exhibition (venue: poster exhibition)

10	17.45-17.55	Václav Jehlička	Chairperson of Committee on Education, Science, Culture, Human Rights and Petitions, Senate of the Parliament of the Czech Republic

June 1, 2006 **Venue: Panorama Hall, Prague Congress Centre**

Session I - Innovative Applications and New Ideas: Movable Heritage
Chairperson: Elin Dahlin (Norway)
Rapporteur: Jean-Marc Vallet (France)

1	9.00-9.15	Charlotte Björdal (SE)	Bacterial destruction of wooden cultural heritage
2	9.15-9.30	Rebecca Ippoliti (IT)	New restoration technique for waterlogged archaeological wood
3	9.30-9.45	Ilaria Degano (IT)	A multi-analytical approach to determine organic dyes in tapestries
4	9.45-10.00	Francesca Piqué (USA)	Methodology for the identification of organic materials in wall paintings
5	10.00-10.15	Terje Grøntoft (NOR)	An early warning system for organic materials in museums, historic buildings and archives
6	10.15-10.30	Joel Taylor (UK)	Dependency modelling for cultural heritage
7	11.00-11.15	Nigel Blades (UK)	Experience and application of the "IMPACT" air pollution software toll to cultural heritage
8	11.15-11.30	Pavel Zítek (CZ)	Impact of moisture sorption stabilization as a preventive conservation approach
9	11.30-11.45	Vasilike Argyropoulos (EL)	Sustainable conservation for metal objects from the Mediterranean Basin

10	11.45-12.00	Carl Johan Bergsten (SE)	Corrosion of lead and lead-tin alloys of organ pipes in Europe
11	12.00-12.15	Albert Canals (ES)	Radiofrequency identification for movable heritage management
12	12.15-12.30	William Wei (NL)	A new non-contact fingerprinting method for the identification and protection of objects of art and cultural heritage against theft and illegal trafficking
13	12.30-12.45	Isabel Rodriguez-Maribona (ES)	Development of a new anti-graffiti system, based on traditional concepts

Session III - Innovative Applications and New Ideas: Cities, Villages and Landscapes (incl. Archaeology)
Chairperson: Takayoshi Yamamura (Japan)
Rapporteur: André Loits (Belgium)

1	14.00-14.15	Paul Vandevelde (BE)	A risk-based approach to cultural heritage buildings
2	14.15-14.30	Paulo Lourenço (PT)	Reducing the seismic vulnerability of cultural heritage buildings
3	14.30-14.45	Federico M. Mazzolani (IT)	Earthquake protection of historical buildings by reversible mixed technologies
4	14.45-15.00	Maurizio Indirli (IT)	Evaluation of multiple risk and building vulnerability in the historic part of Valparaiso, Chile
5	15.00-15.15	Brian Clancy (UK)	Condemning and demolition of older residential property and the resulting break-up of long established communities.
6	15.15-15.30	Guido Carrai (IT)	Research-based municipal policy saves European cultural heritage: case study of Brandýs nad Labem - Stará Boleslav in the Czech Republic
7	16.00-16.15	Ina Macaione (IT)	From cultural heritage to sustainability: Architecture and Nature-City
8	16.15-16.30	Donovan Rypkema (USA)	Socio-economic impact of cultural heritage assets
9	16.30-16.45	Elisabeth Dumont (BE)	Pro-active management of the impact of cultural tourism upon urban resources and economies
10	16.45-17.00	Yosuke Fujiki (JAP)	A study on the method for extraction of tourism-impact on a historical townscape
11	17.00-17.15	Stephen Shaw (UK)	Tourism and multicultural heritage in the enlarged Europe: tools for participation by low-income residents
12	17.15-17.30	Maria Ruiz del Arbol (ES)	A meeting point for diversity: research and valorisation on cultural landscapes in the NW Iberian peninsula
13	17.30-17.45	Nigel Blades (UK)	Impacts of crushed rock quarries on historic villages and cultural landscapes
14	17.45-18.00	Jacques Teller (BE)	Urban and architectural integration of archaeological vestiges

June 1, 2006	Venue: Room Club E, Prague Congress Centre		

Session II- Innovative Applications and New Ideas: Immovable Heritage
Chairperson: Linda Krage (Latvia)
Rapporteur: Roman Kozłowski (Poland)

1	9.00-9.15	Cristina Sabbioni (IT)	Mapping climate change and cultural heritage
2	9.15-9.30	Fulvio Zezza (IT)	Salt crystallization and damage to monuments
3	9.30-9.45	Barbara Lubelli (NL)	Hygric dilation behaviour of NaCl contaminated lime-cement mortar
4	9.45-10.00	Hamid Raad (AT)	Archeometry and the case study of the Nabatean Mortars
5	10.00-10.15	Yves Vanhellemont (BE)	A proposal for test procedures for injection products against rising damp
6	10.15-10.30	Antonella Grossi (IT)	Assessing compatibility in conservation of masonry structures in archaeological sites
7	11.00-11.15	Piero Tiano (IT)	Effects of weathering on stone materials: assessment of their mechanical durability
8	11.15-11.30	Claire Moreau (FR)	How to assess the efficiency of a stone consolidant - the example of the Bologna Cocktail
9	11.30-11-45	Wolfgang Krumbein (DE)	BIODAM - Practicability studies, application experience and success control of polyphasic approaches to inhibit subaerial biofilm growth and damage on buildings
10	11.45-12.00	Francesca Cappitelli (IT)	Biotechnologies and cultural heritage
11	12.00-12.15	Vladimír Kučera (SE)	Tools for assessment of corrosion and soiling in a multi-pollutant situation
12	12.15-12.30	Karl H. Becker (DE)	Atmospheric change and impact on monuments of cultural importance
13	12.30-12.45	Jim Williams (UK)	Foundation re-use as a mechanism for the preservation of buried cultural heritage in urban centres: how new engineering research helps limit archaeological damage.

Session IV - Research Infrastructure - Sustainable Scientific Impact of EC Research Projects on Movable and Immovable Heritage
Chairperson: Ioanna Papayianni (Greece)
Rapporteur: Paulo Lourenço (Portugal)

1	14.00-14.15	Jana Kolar (SI)	Infrastructures for cultural heritage
2	14.15-14.30	Loic Bertrand (FR)	Recent developments of cultural heritage interface at the SOLEIL synchrotron
3	14.30-14.45	Lucile Beck (FR)	Transnational access to the Louvre accelerator facility for ion beam analysis of the European culture heritage
4	14.45-15.00	Brunetto G. Brunetti (IT)	MOLAB (Mobile Laboratory): a transnational access service for in-situ non-invasive studies of the European cultural heritage
5	15.00-15.15	Stanislav Pospíšil (CZ)	Wind tunnel modelling in conservation
6	15.15-15.30	Vasco Fassina (IT)	CEN/TC 346 Conservation of Cultural Property

7	16.00-16.15	Ruven Pillay (FR)	Database management and innovative applications for imaging within museum laboratories
8	16.15-16.30	Mona Hess (DE)	Fragmentary mural paintings – possibilities of aesthetic presentation and exemplary communication
9	16.30-16.45	Wolfram Kloppmann (FR)	Isotope (sulphur, oxygen, boron) tracing of internal or external origin of sulphates involved in the degradation of French stone monuments
10	16.45-17.00	Fabian Käser (CH)	Life expectancy prediction of solid materials using chemiluminescence to characterize oxidative reactions and model-free simulation based on experimental data
11	17.00-17.15	Jaroslav Valach (CZ)	Enhanced optical methods for analysis of historical objects
12	17.15-17.30	Gabriel Maria Ingo (IT)	Large scale investigation of bronze archaeological artefacts from the Mediterranean basin
13	17.30-17.45	Annemie Adriaens (BE)	Monitoring the conservation of metal objects: evaluation of a new approach
14	17.45-18.00	Katarzyna Komar (PL)	Techniques for cultural heritage research in the Pomerania region

June 2, 2006 **Venue: Spanish Hall, Prague Castle**

Session V - Impact of EU policies and directives on European cultural heritage diversity and sustainable safeguarding; impact of cultural heritage research results on society and support for policy needs

Chairperson: Terje Nypan (Norway)
Rapporteur: Johanna Leissner (Germany)

1	9.00-9.15	Terje Nypan (NOR)	The challenge of EU policies for cultural heritage: Impact of EU Directives?
2	9.15-9.25	Jacques Akerboom (NL)	Impact of EU directives on small enterprises acting in cultural heritage field - Monumentenwacht experience
3	9.25-9.35	Chiara Nesti (IT)	Preservation of the cultural heritage of property through an analysis of European regulations. The example of natural bondings
4	9.35-9.45	Francesca Tolve (IT)	An analysis of research projects on conservation of paper and textile artefacts of historical, cultural and artistic value financed under EU Programmes *(Period 1995 – 2005)*
5	9.45-9.55	Ioanna Papayianni (EL)	Applying research results into practice in the field of repairing masonry monuments
6	9.55-10.05	May Cassar (UK)	Towards evidence for policy development in the area of climate change and world heritage
7	10.05-10.15	Monica Martelli-Castaldi (IT)	E.C.C.O - Legal issues of the Conservation-Restoration profession
8	10.15-10.25	Ingval Maxwell (UK)	Fire loss to historic buildings

Session VI- Coordination of National Research & Education
Chairperson: Claudio Modena (Italy)
Rapporteur: Cristina Sabbioni (Italy)

9	10.55-11.05	Piotr Świątek (BE)	Cultural heritage related research at COST
10	11.05-11.15	John Fidler (UK)	Towards an EU-wide strategy for research into the historic environment and its sustainable management
11	11.15-11.25	Sylvie Colinart (FR)	The French national research programme on sciences and conservation of the materials of the cultural heritage: results and future
12	11.25-11.35	Zuzana Bauerová (CZ)	The Czech national research programme on cultural heritage and European integration
13	11.35-11.45	Antonia Moropoulou (EL)	From national to European and international research and education programmes
14	11.45-11.55	Ling Chen (CHINA)	Research on the cultural heritage-based communication and creation models
15	11.55-12.05	Oscar Chiantore (IT)	Training and research at the Foundation Centro "La Venaria Reale"
16	12.05-12.15	Vivi Tornari (EL)	Integration of novel methodologies into teaching practices
17	12.15-12.25	René Larsen (DK)	European Network for Conservation-Restoration Education – ENCoRE: The role of conservation-restoration education in the implementation of European cultural heritage research

Session VII - Challenges of European Cultural Heritage Research
Chairperson: Andrea Tilche (EC DG Research, Head of the 'Environmental Technologies and Pollution Prevention' unit)
Rapporteur: Michel Chapuis (EC)

1	14.00-14.15	Zdeněk Bittnar (CZ) Member of ECTP HLG	Cultural heritage research and the European Construction Technology Platform
2	14.15-14.30	Pétronille Eynaud de Fay (FR), Roko Žarnić (SI) – ECTP FACH Coordinators	Focus area Cultural Heritage in the European Construction Technology Platform
3	14.30-14.45	Caterina Rehm-Berbenni (DE) – FACH HI6 Coordinator	Bridging the gap between research and industry
4	14.45-15.00	Pere Roca (ICOMOS ISCARSAH - ES) ISCARSAH Chairman	Prospects for international cultural heritage research cooperation – ICOMOS initiatives
5	15.00-15.15	Helmut Wenzel (I-SAMCO VCE - AT) Coordinator	International Collaboration on Natural Hazards expected for the 7th Framework Program of the European Commission
6	15.15-15.30	Denis Ricard (OWHC - Canada) Secretary General	Sustainable historical cities – worldwide challenge for interdisciplinary international research
7	15.30-15.45	Jean-Louis Luxen (CHEDI - Culture, Heritage & Development - International) President	Research for historic cities

8	15.45-15.55	Eléonore de Merode (Europa Nostrea) Heritage Awards Co-ordinator	Europa Nostra - message of the President of Europa Nostra, HRH the Prince Consort of Denmark
9	15.55-16.05	José Luis Pedersoli (ICCROM)	Future cooperation of ICCROM with the European Union
10	16.05-16.10	The Getty Conservation Institute	Letter of the director to be presented at the 7th European Conference

Closing Session - Challenges of European Cultural Heritage Research
Chairperson: Cristina Gutiérrez-Cortines (MEP)
Rapporteur : May Cassar (United Kingdom)

11	16.45-17.00	Andrea Tilche (EC DG Research, Head of Unit)	Orientations for cultural heritage research within the Environment Programme
12	17.00-17.35		Conclusion reports from sessions I – VII
13	17.35-18.15		Discussion and future recommendations, 7th FP
14	18.15-18.30		Closing ceremony (reading of conference message)

CONTENTS

Message of the 7th European Conference "Safeguarded Cultural Heritage – Understanding & Viability for the Enlarged Europe" held in Prague May 31st – June 3rd 2006 and organized by the Czech Academy of Sciences with support from the European Commission

The 7th European Conference SAUVEUR, continuing a 20-year tradition of reviewing the outcomes of research into cultural heritage issues, brought together more than 210 oral and poster presentations. The European scientific community demonstrated a remarkable ability to carry out excellent research through effective international consortia, and to work jointly on common problems. The projects were undertaken sometimes with quite modest and fragmented financial support, taking advantage of grants from national research programmes and from other funding mechanisms.

More than 280 Conference participants from 37 countries, including 22 EU Member States, recognise that:

- Environmental change represents one of the main threats to the sustainability of European cultural heritage. Climate change and the increased frequency and intensity of certain natural hazards bring about new performance requirements which are not adequately met by contemporary standards for design and materials. These challenges require innovative approaches and technologies, advanced integrated modelling and optimized use of the research infrastructure.
- In historic settlements, there is a wide range of accumulated problems affecting movable and immovable heritage and related to environmental changes, social impacts, economic issues, growing tourism and inadequate cultural heritage management. Moreover, natural hazards have a much heavier impact on historical settlements than on the modern built environment. Sustainability of historic cities, villages and territories offers a new level of complex challenges. Integrated research into cultural heritage assets related to historical settlements is therefore considered a crucial issue for European countries.
- Cultural heritage research has the potential to contribute even more to the development of advanced environmental technologies through the knowledge generated from basic research and from the adaptation and integration of scientific advances and developments from other sectors, e.g., nanotechnologies. At the same time, there is a great need to strengthen public participation in research, and to communicate more effectively the potential impacts for citizens living in European historic environments. There is a need to establish complementary national research programmes that support effective cooperation in this field, and to apply the ERANET ideas and principles in order to better achieve the Lisbon goals. There is a strong demand from all stakeholders that cultural heritage be mainstreamed into EU and National policies and programmes.
- Research into cultural heritage has a strong potential for harmonizing European policies and for enhancing the competitiveness of industry in various fields, from large construction companies to a wide range of SMEs. The European Technology Platforms, such as the construction platform, play a key role in achieving this goal. The Platforms, all stakeholders and the European Commission need to work together to ensure the widest diffusion and transparency of their work and results.

This Conference invites:

- The European Institutions
  - to give attention to measures ensuring sustainable safeguarding of the European cultural heritage through joint collaborative research utilizing international and interregional programmes,

    - to support the incorporation of cultural heritage themes into all relevant priorities and tasks of the 7th Framework programme, and to intensify their support for cultural heritage research within the 7th Framework Programme,
    - to facilitate ways of overcoming the fragmentation of research for the cultural heritage research community,
    - to ensure that the revision of the EU Sustainability Strategy in 2009 includes explicit mention of the value of cultural heritage research, and
    - to mitigate unintentional negative effects on cultural heritage of EU legislation by carefully applying article 151.4 in all legal documents that are issued.
- The European Research Council (ERC) to consider the importance of basic research for cultural heritage.
- National and regional governments and relevant authorities in Europe to integrate into their research programmes scope for cultural heritage research and support for related research infrastructure.
- Public-private partnerships to be established with the cultural heritage research community, in order to respond to the new and complex challenges referred to above.
- Non-governmental organizations to promote public participation in cultural heritage research, namely related to environment, energy, sustainability and quality of life.

Environmental technologies and pollution prevention

Andrea Tilche

EC, DG Research, Directorate "Environment", Head of Unit

1 Contents of the "Environmental Technologies" sub-priority

The specific aspect of Environmental Technologies forms one sub-part of the Environment Priority. Cultural Heritage is conceived as one part of a wide range of activities that should be carried out within the Environmental Technologies that deal with:

- technologies preventing or reducing environmental risks and disasters;
- technologies promoting sustainable production and consumption;
- technologies for managing resources or treating pollution more efficiently, in relation to water, soil, air, sea and other natural resources, and wastes;
- technologies for the environmentally sound and sustainable management of the human environment including the built environment, urban areas, landscape, as well as for the conservation and restoration of the cultural heritage.

2 Amendments passed by the Parliament and the Council

Recently, the Parliament (the ITRE Committee, not the Parliament as a whole) has approved a series of amendments to the Framework Programme texts. One of these amendments is the same as an amendment introduced by the Council in the so-called "General Approach" to FP7 which is now the text that the Council will present to the Commission and the Parliament for discussion. This new bullet point separates the aspect of Cultural Heritage from all the other aspects of Environmental Technologies and makes it more independently clear. It states: "*Protection, conservation and enhancement of cultural heritage, including human habitat: improved damage assessment on cultural heritage, development of innovative conservation strategies, foster integration of cultural heritage in the urban setting*".

2.1 The Environmental Technologies in the Environment specific programme

The Environmental Technologies sub-priority also includes aspects related to technology assessment, verification and testing that do not deal a priori with CH aspects.

During the preparation and development of the Environmental Technologies part, a series of drivers should be taken into account:

- First of all, there are a number of strategic research agendas of various technological platforms (on water supply and sanitation or other platforms, e.g., the platform on construction, forestry, textiles, etc.),
- A new research programme in wastes must be developed,
- We have to deal also with other Environmental Technologies for a number of other environmental matters,
- Technologies for protecting Cultural Heritage,
- Aspects of Technology assessment (Life Cycle Assessment, risk assessment, which is also connected to REACH –as the new regulation for registration of chemical products),
- Support for various Environmental Thematic Strategies (Soil, Wastes, Pesticides, Management of Resources, etc.),
- The link with the Environmental Technologies Action Plan (ETAP).

2.2 How to design a long-term work programme?

There are a number of different drivers that must be taken into account in building a more or less homogeneous programme within which the section on Cultural Heritage should also be hosted.

But how to design a long-term programme (as the Framework Programme will last 7 years)? For the time being, only the most general documents have been prepared: the "Framework Programme Document" and what we call the "Specific Programme Document", which are the most fundamental texts that I have presented to you. The Commission has therefore decided to proceed with annual work programmes. Each year a work programme will be published for the following year, containing only a few specifications for the subsequent year. However, in the planning exercise this is not enough, because we have to keep in mind what to do in the next 7 years – or at least in the next 4-5 years – as a first starting point in order to be able to decide on what to propose for year 1, year 2, etc.

As background information, it should be noted that we have not yet finalised all the projects of the 5th Framework Programme, which is still ongoing. However, almost all the FP5 projects will be closed this year.

When we start the 7th Framework Programme, we will also have all the 6th Framework Programme projects running, and some of them are now just starting. This means that we have to define a roadmap that is based on critical research needs, but it should also take into account what is ongoing in order to minimize duplication and overlaps.

2.3 How to define critical research needs?

We have passed through a number of steps:
Let me present some of the most recent ones to you:

- The Parliament "Hearing" organised by Prof. Cristina Guttierez on Cultural Heritage research on 6th February 2006, followed by a one-day meeting (February 7th) of a group of experts on belonging to different stakeholder groups, chaired very effectively by Prof. May Cassar. This was a very interesting brainstorming exercise, and it provided significant input and ideas for preparing the WP.
- We have also established an Advisory Group for FP7. The 1st meeting will take place on 15/06 and our commitment is to present the 1st draft of the 2007 Work Programme for the 19 July. It will be quite a hard work in the next few months to meet this deadline with a well-worked out project.
- Fortunately the European Construction Technology Platform (ECTP) and its Focus Area on Cultural Heritage (FACH) has also been working on this topic for quite a long time – nearly a year and a half – and they have already generated some very interesting input for us. This Conference is expected to build on this, reviewing the results of the last two years and identifying research gaps and future needs.

2.4 Budget constraints

However, a first warning is that the budget for the 7th Framework Programme is not what we had initially expected. You probably know that the Commission proposal was to double the budget in comparison with the 6th Framework Programme. However, the discussions in the Council on the 2007-2013 Financial Perspectives have led to a shortfall in our budget, and we now expect, on an average, 30% less than the initial proposed doubling of the funding.

In 2013, the research budget is expected to be 70% more than the 2006 budget. This implies that in order to create this availability of funding we have to build a curve that will be rather flat at the beginning and very steep at the end. That is to say, we will start with a relatively low budget (for the Environment priority this will even mean a lower budget in 2007 than in 2006) and from the 3rd or 4th year we will see a significant growth.

The last point is that we have to evaluate the impact of the new *Rules of Participation*. As you may know, the new Rules of Participation no longer apply the cost model system, so there will be no more additional costs or full cost. Universities and all public bodies will be allowed to apply for 75% of the full costs. This will be extremely positive for them, because they will be allowed to charge permanent staff in the costs.

This also applies for SMEs. This should have a positive effect, as they will be encouraged to participate more in the next FP.

2.5 Now how to make limited funds more productive?

Now how to make limited funds more productive? I am convinced that the impact of research activities is not related only to the available financial resources. At the starting of FP7 there will be a modest rise in our investments in Cultural Heritage research in the sense that we will probably pass from 4 M€/year in 2006 (FP6-SSP5) to about 6-6.5 M€ in 2007-2008. This will then keep growing in the more distant future.

The inputs from this Conference will be therefore of the greatest importance in helping us to decide on how to make the best investments.

We have some questions that I hope you will help us to answer:

- Is it better to continue as with FP6, with well defined, narrowly-focused SSP-type actions (the kind of projects performed in the 6th FP for cultural heritage), or should we invest in broader but less numerous initiatives that may deliver a greater impact?
- Should we define the topics in a top-down (determined) way or should we allow for a more bottom-up approach?

We will be listening very attentively, to hear what you consider best.

2.6 A multiple integrated approach

Cultural Heritage research is excessively fragmented today: there is an absolute need for higher integration and cross-fertilisation among different sectors.
The starting point for us is summarized in the following short statement.
The overarching objective is the Protection, Conservation and Restoration of Cultural Heritage, which requires a multiple integrated approach:

- Focus on complex assemblies and not only on individual materials. CH objects are complex, and are not made of a single masonry type, or of glass or stone. They are assemblies consisting of a number of aspects.
- Damage functions, assessment and monitoring for conservation cannot be divided down and separated out.
- The importance of context in research on moveable and immoveable heritage. Moveable heritage belongs to immovable assets, and vice-versa. They cannot be considered as separate things, so we should achieve better integration between these two aspects that have frequently been in the past considered separately.

3 A tentative roadmap

As a tentative roadmap, we have tried to design some research areas and to put together some ideas about when these research areas might be developed.

- The first is “Diagnosis, assessment and monitoring technologies and tools”, which may be an area to start with next year.
- “Managing environmental change, hazards, damage mitigation and preventive conservation”, during the second year.
- Two other areas: “Cultural Heritage compatible materials” and “Conservation and restoration techniques”. We foresee developing these jointly with another priority within FP7 priority 4 “Nanotechnologies: materials and industrial processes”; in this priority, the available budget seems higher and therefore we will examine the possibility of exploiting synergies by developing joint or coordinated calls with our colleagues who are responsible for following the overall ECTP work much more closely than we can.
- “Protection of archaeological sites and cultural landscapes”.
- Finally “Fostering the integration of Cultural Heritage in the urban / rural setting”.
- This will be supplemented by “Support, training and coordination actions carried out throughout FP7”.

4 Conclusion

We think that a roadmap approach is necessary in order to take stock of the state-of-the-art for building a strategic view of *innovation potential* in the future, and in particular for finding where innovation can have a *higher potential impact*. We should also have in mind that for the first two or three years the budget will be only slightly higher than today, while later it is likely to start growing.

Emphasis will be laid on projects that can demonstrate the highest impact, for instance technologies and methodologies that can be applied to a wide range of cultural assets, within the context of research on Environmental Technologies. A holistic and integrated approach should be encouraged regarding the “moveable” and “immoveable” character of CH assets.

Finally, as the last consideration, there are some opportunities that can be offered by other parts of the 7th Framework Programme: the ICT priority, the Socio-Economic and Humanities priority, as well as the new European Research Council, which will support basic and fundamental research, the Marie Curie fellowship programme (the “People” programme) for which the budget will be substantially increased. This programme will support very interesting new schemes linking industry and academia, and this will be of particular interest for SMEs.

So, I conclude my presentation by repeating to you that your feedback and the results of this conference are of the highest value for us.

Session I

Innovative applications and new ideas: movable heritage

Bacterial destruction of wooden cultural heritage

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Key words: bacteria, decay, wood, waterlogged, foundation poles, archaeological wood, preservation, in situ

Abstract
BACPOLES was a cross disciplinary research project within the 5th framework. It both involved archaeologists, wood scientist as well as molecular microbiologists. The objectives were to isolate and identify the unknown type of bacteria, that are the main degraders of waterlogged wood, and also to test the novel idea of using bacteriophages against wood degrading bacteria to protect wooden cultural heritage from decay. At the end of the 3 year project, we had managed to develop an isolation technique for these unknown types of bacteria, and by help of modern molecular techniques it was concluded that the wood degrading bacteria most likely belonged to the Cytophaga group. The relation between decay speed and environmental parameters was also investigated and found highly complicated.

Today, spin off effects from the BACPOLES are implemented into different areas for the protection of wooden related cultural heritage. Typical objects are: wooden pilings supporting historical building; shipwreck; old track ways; and wetland settlements. The problem exists in several European countries. At the site BRYGGEN in Norway, which is protected by UNESCO, the historic buildings are running the risk of sinking into the soil because of uncontrolled microbial deterioration. A bronze age track way in Somerset levels, UK, and the remains of the fortified settlement Biskupin in Poland, may disappear. The historic building in Venice may suffer severe damage if the strength of the wooden foundation pilings is lost. Thanks to BACPOLES we are now one step further in understanding and protecting these valuable sites. Future work will focus on environmental friendly preservation methods that can be tested at several historical sites in Europe.

1 Introduction

1.1 The “BACPOLES” project

From 2002 to 2005, the European Commission funded a scientific project with the title: “Preserving cultural heritage by preventing bacterial decay of wood in foundation poles and archaeological sites”. BACPOLES was the acronym for this multidisciplinary research project, which involved archaeologists, dendrochronologists, wood scientists, microbiologists, soil scientists, and engineers from 5 different EU countries (The Netherlands, Sweden, Great Britain, Germany and Italy) and 11 institutes and universities.

BACPOLES was established within the 5th frameprogramme; Thematic programme IV: Energy, environment and Sustainable development; Key action 4: City of tomorrow and Cultural heritage; Sub action 4.2.1: Improved damage assessment on cultural heritage. The EU no is: EVK4-2001-00009.

1.2 Background

1.2.1 Wood in a historic context

Wood has throughout history served as an important raw material for mankind. Larger constructions like houses, track-ways, bridges and boats, as well as smaller objects like furniture, weapon and tools have been produced by generations since ancient times in most cultures. One could say that wood provided the foundation for development of human cultures. In theory, wooden objects should constitute the largest group of archaeological finds in our museums, but this is not the case. Like most organic material, wood undergoes a fast decomposition in nature. In Europe, the only remaining archives of wooden archaeological remains from the past, are the findings in terrestrial and aquatic waterlogged environments, where artefacts or constructions by accident or on purpose has been surrendered by our ancestors.

1.2.2 Wood degradation

In the past, two main causes of wood decay were known; – one initiated by fungi and the other initiated by insects. In sea, additional decay was caused by marine organisms (*Limnoria, Teredo*) which had a fast and aggressive impact on wooden poles in harbours and not at least the wooden vessels [1]. Most wood degraders are, however, highly dependent on access to oxygen and nutrients for active decay, and therefore wood has in general being considered safe in low oxygen water-saturated environments. During the last decades this statement has been questioned, reconsidered, reinvestigated, and finally a new hypothesis have been suggested.

In the 1960's, severe strength loss of foundations poles supporting historic buildings was reported [2, 3]. Despite that they were submerged in water and soil, the surface was soft and weak. The decay could not be explained by fungal attack and therefore bacterial degradation was suggested, but could not be verified with certainty. First in the 1980's, with help of high resolution electron microscopy, bacteria were found degrading wood cell walls [4, 5]. It became clear that bacteria could degrade wood at very low oxygen levels and investigations of foundations poles and archaeological wood in the years that followed showed that the bacterial decay was a widespread and common decay phenomenon in waterlogged environments [6, 7].

1.2.3 Erosion bacteria

The bacteria were named by their way of eroding the wood cell walls (Fig. 1). The decay starts at the wood surface and proceeds slowly inwards through the anatomical openings in the micro-structures of the wood [8]. They are specialised in utilizing the holocellulose from the lignocellulosic matrix of the wood cell walls as a nutrient. Their decay causes losses in wood mass and strength. A morphological transformation of the cell walls and specific decay patterns can be seen using light microscopy (Fig. 2). Despite many attempts during the last decades, it has not been possible to isolate and identify the bacteria species.

2 Description of problems

2.1 Foundations poles supporting historic buildings

In past times and even today, foundation piling has been a useful engineering technique for constructing support foundations for houses, buildings, bridges, and track-ways in areas with weak soil (Fig. 3). Venice as well as cities in the Netherlands, Germany, Poland, and the Scandinavian countries are examples where this technique has been most frequently used.

Over the last three decades an increasing number of wooden foundation poles have been found with serious decay. Rotten poles have been reported from different locations in Europe. Some well known examples include the historic buildings in the Old Town of Stockholm (Sweden); the Reichtagshaus in Berlin (Germany) [9]; and Haarlem in the Netherlands, where recent research revealed that about 1000 houses are in need of new foundations or foundation repairs. The problem of Venice highlights the situation further. Here tens of millions of poles support the city (e.g. 1.150.657 piles under the Santa Maria Della Salute Church and 120.000 elm piles under the Rialto bridge). The situation becomes most problematic when the sediment normally surrounding and protecting the piles, is eroding away, leading to exposure to oxygenated water and a more decay prone environment (Fig. 4). However, a full inventory of the impact of bacterial deterioration on the wood foundation poles has not yet been carried out, neither on a national or European scale. For some of these buildings, preservation plans and innovative techniques are most urgent.

2.2 Archaeological wood

In waterlogged environments, archaeological wood is often found well preserved in contrast to drier sites, where the only remaining evidence of historical wood may be a black contour of decomposed wood in contact with the soil. While still wet, well preserved archaeological wooden objects retain their dimensions and integrity. Ornamentation and tool-marks are often intact in the surface layers (Fig. 5). The soft swamplike condition, when pressed, reveals however a very fragile inner structure. Until the 1980's, decay of waterlogged archaeological wood was believed to be of chemical origin. But when this special type of wood became a matter of interest for wood scientists, it was soon revealed that bacteria were the main degraders.

During the 20th century several unique shipwreck, settlements and track-ways has been found through out Europe. The fortified settlement Biskupin in Poland [10]; the ancient lake settlements in central Europe [11]; the sacrificial peat Nydam in Denmark [12]; the stone age settlement Alvastra in Sweden; a huge amount of shipwrecks in the Netherlands, U.K and the Scandinavian countries, just to mention some examples. Very often, these large constructions has been left in situ for future considerations, due to the huge costs for excavation, conservation. This lack of preservation strategies could be devastating for future generations and for future multidisciplinary research on past times. Archaeologists investigating the numerous prehistoric trackways and settlements in the Somerset moors, have recently forecasted the destruction of all historic wooden material in the wetlands before the end of this century (British archaeology, issue 63, Feb 2002).

Lately, reburial of archaeological timber has been regarded as an alternative option to conservation of larger wooden constructions [12, 13, 14]. Excavated wood is then reburied in a natural environment regarded as more protective than the original site. This technique is still embryonic and the effect hardly documented or reported.

2.3 Consequenses for future generations of European citizens

The effect of bacterial decay on wooden material has two main consequences for society:
1. Huge economical costs of replacing foundation poles supporting historical buildings.
2. Irreplaceable loss of cultural heritage at archaeological sites.

3 Aim and objectives

3.1 Aim

Wood in cultural heritage and especially in an archaeological context is vulnerable to bacterial degradation. In order to preserve unique cultural heritage for future generations, it is important to find ways to stop the degradation process.

3.2 Objectives

Little is known about the process of bacterial degradation and it has not been possible to isolate or identify any of the wood attacking bacteria despite several attempts during the last decades.

The main target of the BACPOLES project was therefore to identify the erosion bacteria by help of the combination of isolation, culturing and advanced molecular DNA technology. Based on the identity of the bacteria, novel biological methods using bacteriophages should be developed and tested for their effect to kill the bacteria and stop decay.

The degree of decay in wood samples from 24 BACPOLES sites around Europe was related to its environmental parameters. The data from all sites were analysed in order to identify single factors in soil and water that either promote or inhibit bacterial decay. This was important basic research work, that will be essential for development of preservation techniques in situ and for reburial applications.

4 Outcome of the BACPOLES project

4.1 New information obtained by the BACPOLES project

4.1.1 Erosion bacteria decay and environment

The investigations were carried out on waterlogged wood retrieved from 24 archaeological and historical sites in Europe. As result of intensive laboratory work on culturing active erosion bacteria from 89 wood samples, followed up by advanced isolation procedures, the final DNA/RNA analyses suggested that the active wood degraders present in the historic wood belonged to the CFB (Cytophaga-Flavobacteria-Bacterioides) group of bacteria. Evidence was found for several species of erosion bacteria with varying morphology. All rod shaped, but with a length varying between 1-10 µm. Each species may have its own environmental amplitude, which explains the presence of active erosion bacteria in a wide range of different environmental conditions.

Low nitrogen and oxygen concentration seemed to promote the degree of decay and in general, erosion bacteria seem adapted to environments low in inorganic nutrients.

4.1.2 Actual decay rate in Europe

The erosion bacteria were found to be active and alive in wood at all 24 sites in Europe. This suggests that the decay process is ongoing at this very moment. Even in wood samples of considerable age (2500 years old).

4.1.3 Methods for preservation

The methods and substantial knowledge obtained from the environmental observations, suggests several different physical and chemical environmental factors that are important for the activity of erosion bacteria. In combination with the promising preservation techniques tested already under laboratory conditions in BACPOLES, it is now possible to test at least some promising approaches in both laboratory and field before the final techniques can be applied on archaeological sites.

4.1.4 Development of laboratory technique for testing environmental parameters and effect of preservation methods

Development of microcosm systems in laboratory was most valuable for all experimental work. Here, soil, sediment or water from different archaeological sites could be used to investigate bacterial wood decay under controlled conditions in the laboratory. The effect of different environmental parameters, like nitrogen and oxygen, and other factors that increased or decreased bacterial degradation were monitored. The microcosm set up, developed in BACPOLES, is a key technique for the future studies on the effect of in situ preservation methods.

4.2 The final BACPOLES report

The outcome of the BACPOLES project is described in its full length the final report EVK4-CT-2001-00043. Here all information on material and methods as well as the results can be obtained. Furthermore, a publication process is ongoing, and most results will be published in scientific journals for the benefit of the international scientific society.

5 Conclusions and future work

There is a great need to prevent the bacterial degradation and to protect the cultural heritage from further deterioration. Decay by erosion bacteria is found in waterlogged wood world wide and the process is ongoing. Therefore this project as well as the forthcoming future research will benefit not only the preservation of European cultural heritage, but have a great international application.

5.1 In situ preservation of important archaeological sites is urgent

All over Europe, many unique historic settlements from stone-age and forward are in desperate need for an active rescue plan. The global climate change is likely to influence previously stable conditions. In the autumn 2005, the BBC news highlighted a British study showing the ultimate loss of two late prehistoric wooden trackway on the Somerset moors. Due to periodic drying up of the upper 40 cm of the wetland, the wood had damaged by desiccation and a total disintegration had taken place. Several more Neolithic track ways were in danger (BBC News 7 oct. 2005). The Neolithic lake settlement Alvastra in Sweden, is at present preserved in a wetland area, but the future preservation potential is unknown due to drainage of the area and the ongoing wood degradation. The Nydam sacrificial pond dated iron-age, has recently been a topic for an in situ preservation project in Denmark. The wood is found heavily degraded by bacteria and further more; wild plants (*Equisetum* species) with long roots are penetrating the softened wood material. Original wooden constructions of the fortified settlement in Biskupin, Poland, are partly exposed in open air and risk a fast biological decay process if no protection technique is applied (Fig. 6). In Slovenia settlements in Ljubljanska barje is dated 4th to 3rd millennium BC. The unique constructions of pile dwellings are still present, and can be studied by research teams, but drainage and wood decay is a great threat for the continued preservation [15]. Despite several national attemps to save important historical sites, no country has so far developed preservation strategies or plans. The failure just reflect the very complicated research field, which probably need a multinational research group of specialists for further success.

The scientific outcome from the BACPOLES project now provides Europe with knowledge, methods and technique for development of advanced preservation techniques to protect this unique cultural heritage from degradation in order to save it for forthcoming generations.

5.2 Foundation poles supporting historic buildings

Both the late medieval settlement town Bryggen (the old wharf) in Norway, and the city of Venice in Italy, are so unique that they are protected by UNESCO. Venice is built on poles just as many historic buildings in Europe, and the houses at Bryggen rest on mostly wooden remains. Due to bacterial degradation, the wood slowly looses its strength which often lead to severe movements of the construction as well as crackings and un-controlled sinking. Until the 1950's all buildings in the European estuary area, were erected on wooden foundations. The use of wooden foundation piles is most known from the Netherlands where 25 million piles still are in service and about ¼ of all piles are under threat of bacterial decay. It is calculated that this represents 20-30 billion euro for repair activities. BACPOLES increased the knowledge on the process of bacterial degradation and provided in this way new possibilities to stop the process of bacterial wood degradation. The Netherlands are unique by their wide possibilities to install field tests of preservation methods and for their urgent need to protect its cultural heritage and family houses standing on wooden piles.

5.3 Future preservation methods

From the data and knowledge obtained by the cross disciplinary research team in the BACPOLES project, three innovative techniques with different approach have been identified as promising methods for continued development and practical use. The methods should be tested both in microcosms (developed by BACPOLES) as well as in field. The methods suggested, are variations and a combination of conventional and novel biotechnical techniques.

1. The first method demands initially a full description of the site parameters and a DNA-identification of the consortia of erosion bacteria present in the wood. With help of advanced biotechnology, one specific phage, who is able to infect and kill a specific wood degrading bacteria, can be produced in laboratory and multiplied. If larger consortia of erosion bacteria are present, a specific mixture of phages will be produced. The preservation effect will be monitored by methods developed in BACPOLES during tests in laboratory and field. Finally commercial phage-based wood preservative, an environmental friendly biological "vaccine", can be developed.

2. The second method was established as a spin off effect from the observations made on the hydrology and water flow within and around the wood material. There were strong indications showing that the bacterial decay increased with high water flow. The idea of this method is therefore to impregnate or encapsulate the wooden structures (piles or archaeological construction) at site in order to close the wood structures and exclude the water movements within the wood.

3. The third approach will be to develop new environmental friendly wood preservatives, specific for bacterial attack.

5.4 Impact from BACPOLES

In the project, methods were developed for culturing wood-degrading bacteria from wooden foundation poles and archaeological wood. These methods may be used by microbiologists and molecular biologists for final identification of the species of bacteria responsible for the decay. Idenftification and a better understanding of their physiology will facilitate development of preventive measures.

Bryggen in Norway suffers from complicated and not fully understood decay in the old wooden remains that in part forms the foundation for the buildings. The problems have been realized during the last two year and a research and preservation plan is forthcoming. During this process, knowledge and results from the BACPOLES project have been of great value and some of the BACPOLES partners are now involved in the continued work of preserve this unique cultural heritage.

In the Netherlands, the BACPOLES project was highlighted in the national newspapers and radio. This interest most likely reflected how common this problem is for the dutch people and their houses. Still, BACPOLES partners plays an important role, on a national level, in the discussion of future strategies regarding foundation poles, preservation in situ and reburial of wooden objects.

6 Acknowledgement

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New restoration technique for waterlogged archaeological wood

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Key words: waterlogged wood, restoration

1 The new Arkè technology applied to waterlogged wood restoration

Contento Trade srl, together with LMTAI of La Rochelle University, France, developed a new restoration technique called Arkè technology, using starch impregnation and DDCV desiccation treatment.
This methodology consists in 4 main treatment phases:
1. Evaluation of the degradation level of the wood
2. Impregnation of the wood with modified starch
3. DDCV treatment
4. Final equilibration

To these phases it's possible to add a fifth one for the improvement of the museal exposition of the treated object, so it includes the superficial treatment of the object and a structural consolidation.

1.1 Evaluation of the degradation of the wood

The determination of the wood degradation it's fundamental to plan an adequate restoring intervention. It's necessary to identify two characteristics of the wood: the wood species and determination of the Maximum Water Content (MWC).

The MWC specifies the degradation of the wood, expressed as percentage ratio between water and wood under complete saturation conditions. In the waterlogged wood this ratio shifts between 120 % to 800 % but can exceed the 1.000 %. Arkè technology is suitable for the treatment of wood objects with a maximum water content inferior to 600 %.

1.2 Impregnation of the wood

The starch has been chosen as impregnating agent, eventually combined with other polysaccharides with shorter chain (dextrin, sugars). This mixture of consolidating agents polymerises forming structures similar to the cellulose that pre-existed in the wood before the submersion period. Moreover these mixtures are able to reach the inner layers of the waterlogged wood in a short time.

The composition and the concentration of the impregnating solution is chosen on the basis of the wood degradation level.

The impregnation takes place at room temperature and with a slow agitation of the impregnating agent and can be done inside a treatment chamber or in a mixing chamber depending on the dimension of the wood, the degradation level and of the wood specie.

The material obtained by the consolidation can have a density very similar to the wood before the submersion, because the starches mixtures does not saturate completely the wood structure but reinforces it by sticking to the cellular walls of the wood.

Another advantage of this treatment is the nearly total reversibility: in fact it's possible to recovery the 95% of the impregnating mixture thanks to a simple washing of the wood with water.

Moreover the new "starch-wood" structure created with this treatment has interesting durability features and does not seem to be attached by biological agents at temperature and humidity characteristics typical for museum expositions.

Actually new studies are running to try to explain this phenomenon but, in any case it's possible to inject, with the starch, also anti-fungi and anti-bacteria agents inside the wood structure.

1.3 DDCV treatment

This treatment is aimed to:

- Gently remove the water from the impregnated wood;
- Minimize shrinkage and collapses during the water removal;
- Polymerize the starch based impregnating agents;
- Debacterize completely the treated object.

The wood elements are heated in a process chamber by convection with a mixture of air and steam at controlled pressure, temperature and moisture.

Water removal is obtained by several drops of pressure which cause the vaporization of the liquid heated water present in the wood. An important formation of aerosols increases the efficiency of the water removal process.

An important feature of this treatment is the possibility to shape the wood during and after the water removal phase, simply adjusting the heating fluid: this fact guarantees a complete reversibility of any structural inconvenience especially those related to big size elements.

1.4 Final equilibration

The last step of the Arkè technology is a thermal treatment carried out at atmospheric pressure under controlled relative humidity and temperature conditions in order to prepare the wood elements to their future exposition.

Arkè technology is perfectly suitable for valuable wood findings.
The wood is maintained under vacuum (30-800 mbar) at room temperature when its MWC is < 600 % , while for the most ruined elements it's running a study for an application that foresees a pressure range between 0.5 and 100 millibar, combining the instantaneous freezing of the wood element with its dehydration. Both these treatments can be applied inside the treatment chamber.

The advantages of DDCV system compared to others desiccation processes actually on the market are:

- de-humidification of the treated sample at room T (or at low T) to contrast the collapse of the structure with intermittent and cyclic decompressions
- the treatment is the most rapid compared to all the others, suitable both to impregnated and not impregnated woods
- the treatment needs energy consumption inferior to freeze drying and desiccation under vacuum treatments.

The results obtained with our innovative method can be observed in the following photos.

Figure 1: Before Arkè treatment

Figure 2: After Arkè treatment

The first large size pilot plant is located in Salerno (Italy) and is able to treat wood objects and elements of any kind of essence with a Maximum Water Content (MWC) < 600 % and with dimension of 5 × 1 × 1 meters.

2 Conclusion

The Arkè technology is based on the research carried on during a *Craft WEST project*, funded by the EC (Wood Exploitation by using Starch Impregnation and D.I.C. Technology, n. ENV 4 CY 98 0767), that aimed at treating the waterlogged wood.

Figure 3: Running impregnation chamber

Afterward the technology was improved and exploited at industrial level with a national project funded by the Italian Ministry of Research. This technology is patented.

From these projects a new company, “Legni & Segni della Memoria” in Salerno (IT) was created. There, an complete industrial plant for the treatment of archeological waterlogged wood has been built. This restoration center has already restored many roman boats, a pirogue, some wood statues and other important archeological wood objects, in accordance with Italian Monuments and Fine Arts Bureau.

Now on the market there is a new, successful technology that has the following positive aspects:

- Surprising aesthetic results
- Consistent reduction in treatment duration
- Complete reversibility of the treatment
- Re-building of a wood structure similar to the original one
- Satisfying resistance to fungi and bacterial attack
- Ecological: no solvent use and low energy consumption
- Possibility to treat big dimension objects

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A multi-analytical approach to determine organic dyes in tapestries

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Key words: GC-MS analysis, HPLC-UV-Vis analysis, organic dye, aged textiles, conservation

1 Introduction and content

Studying the materials used in textile dyeing may considerably help in understanding how an object itself originally looked and in dating and locating its origin. Furthermore, recognising colouring matters in old textiles is difficult due to the wide range of substances used for dyeing purposes (the main chromophores in natural dyes are flavonoids, anthraquinones, tannins and indigoids [1]), to the poor light fastness of some molecular markers and to the complexity of the degradation processes, which are not yet completely clarified [2].

Thin Layer Chromatography was employed first for the separation and identification of natural dyes [1]. Besides Wouters *et al*. [3, 4] the standard method for the analysis of organic dyes is Reverse Phase High Pressure Liquid Chromatography (RP-HPLC) with the aid of a spectrophotometric UV-Vis detector. The method was implemented by the introduction of diode array [5-17] and mass spectrometric detectors [18-24]. In the study of natural dyes, gas chromatographic techniques have not been exploited much, due to the relatively high-molecular mass and polarity of the target compounds [25]. Derivatisation of the components of the fibre extract is thus mandatory. Nevertheless, due to the high anti-oxidant activity of flavonoids, gas chromatographic techniques have been widely used for the evaluation of their occurrence in plants and also in biological fluids, after a suitable derivatisation step [26-28].

To bypass any sample pre-treatment, pyrolysis-GC-MS in the presence of a derivatising agent [29, 30] and DE-MS [31, 32] have also been tentatively used.

We have approached dye sources characterisation by a multianalytical point of view. Research has focused on chromatographic techniques, namely RP-HPLC with UV-Vis detection, and GC-MS in order to separate and detect stable molecular markers typical of different dye sources, surviving in old textiles.

The most significant results of some samples from a XVI century tapestry, kindly provided by the "*Laboratorio di restauro degli arazzi*" (Opificio delle Pietre Dure, Florence), are presented.

2 Materials and methods

2.1 Reagents

All the solvents were Carlo Erba (Milan, Italy) pesticide analysis grade, except from ethyl acetate (AcOEt), Anala R, BDH. Hexadecane, used as internal standard, and N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane were purchased from Sigma (Milan, Italy). Standard solution of chromophores in methanol were prepared from gallic acid (99%), ellagic acid (97%) and luteolin (97%) from Lancaster (Great Britain); purpurin (80.9%), apigenin (≥ 95%), kaempferol (≥ 95%) and fisetin (99%) from Fluka; alizarin (97%) and carminic acid (90%) from Sigma. All reagents and chemicals were used without any further purification.

2.2 Reference materials

The following reference raw materials were purchased from Kremer-Pigmente (Germany): weld (*Reseda luteola L.*), flowers and dried leaves; young fustic (*Cotinus coggygria*), bark pieces. Reference Madder lake was purchased from "Zecchi Colori belle arti restauro" (Florence, Italy). Reference cochineal was kindly provided by Mrs. Cheryl Porter, and Indigo by the Opificio delle Pietre Dure.

2.3 Samples

Some samples from "*Giuseppe fugge dalla moglie di Putifarre*" tapestry, shown in figure 1, were kindly provided by the "*Laboratorio di restauro degli arazzi*" (Opificio delle Pietre Dure, Florence). Bronzino made this tapestry's cartoon around the half of XVI century, and the weaving is due to Karcher's atelier [33]. Samples weight around 0.5 mg, and are listed in tab. 1.

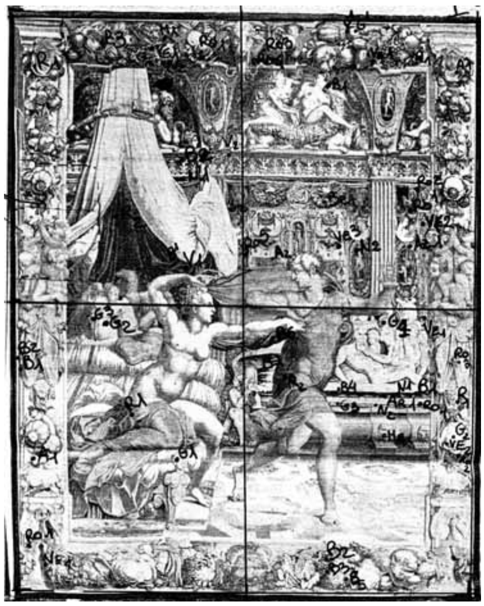

Figure 1: "Giuseppe fugge dalla moglie di Putifarre", black and white photograph

Table 1: List of samples

Sample	Colour
I Ro1	Red
I Ro1*	Red (light)
I Ro3	Red
I Ro4	Red (light)
I Ro5	Red
I G1	Yellow (golden)
IV G1	Yellow
I Ve1	Light green
I N1	Brown (dark)
I N2	Black

2.4 Apparatus

2.4.1 High performance liquid chromatography

An HPLC consisting of a PU-2089 Quaternary Gradient Pump with degasser (Jasco International Co., Japan), equipped with a Rheodyne Model 7125 injection valve and coupled to a spectrophotometric UV-Vis detector UV-2075 (Jasco International Co., Japan) was used. The signal was acquired by an ACI (Dionex) interface and the data were processed by Dionex PeakNet® software. The chromatographic separation was performed on an analytical reverse phase C-18 column (Wakosil II 5C18RS, 5 µm, 250 × 4.6 mm, SGE International, Australia) connected to a C-18 pre-column (1 mm Opti-Guard C18, Optimize Technologies Inc., Oregon, US). The eluents were: A, acetonitrile with 0.1% trifluoroacetic acid; B, water with 0.1% trifluoroacetic acid. The eluition programme for red dyes is described elsewhere [34]; for yellow, blue and dark dyes the programme is: t = 0-15 min, flow rate = 1 mL/min, eluent A 25%, B 75%; t = 15-30 min, flow rate = 0.9 mL/min, gradient from A 25% and B 75% to A 50% and B 50%; t = 30-40 min, flow rate = 1 mL/min, gradient from A 50% and B 50% to A 90% and B 10%. UV detector wavelength: 275 nm.

2.4.2 Gas chromatography

A Trace GC gas chromatograph (Thermo Electron Corporation, USA) equipped with a PTV injection port and a mass spectrometric detector based on an ion trap analyzer (Polaris Q, Thermo Electron Corporation, USA). The PTV injector was in the CT 'splitless with surge' mode at 280 °C with a surge pressure of 100 kPa, and the mass spectrometer parameters were: electronic impact ionization (70 eV), ion source temperature 230 °C, scan range m/z 50–700 and interface temperature 280 °C. Chromatographic separation was performed on a DB-5MS chemically bonded fused silica capillary column (0.25 mm i.d., 0.1 µm film thickness, 30 m length, J&W Scientific, Agilent Technologies) with 5% phenyl–95% methylpolysiloxane stationary phase. The gas chromatographic conditions were as follows: initial temperature 57 °C, 2 min isothermal, then ramped at 10 °C/min up to 200 °C, 3 min isothermal, then ramped at 20 °C/min up to 300 °C and then isothermal for 20 min. The carrier gas was He (purity 99.9995%), at a constant flow rate of 1.2 mL/min. Peak assignment was based on comparison with analytical reference compounds and materials, with library mass spectra (NIST 1.7) and with mass spectra reported in the literature.

2.4.3 Direct exposure mass spectrometry

Direct Exposure-Mass Spectrometry (DE-MS) technique is based on the direct introduction of the sample in the mass spectrometer. The sample, after its introduction into the ion source, is desorbed from a Rhenium filament by controlled heating and is ionized by electron ionization impact. Thus, it is possible to obtain a graph representing the total ion current (TIC) in function of the time (that is, of temperature) and a set of mass spectral data, averaging the mass spectra in the desired time range. Mass spectrometer parameters were: electronic impact ionisation (70 eV), ion source temperature 230 ºC, scan range m/z 50-650. Negative ionisation mode was selected due to the electronegativity of the oxygen atoms present in the anthraquinones: it allows a better selectivity for the target compounds to be achieved thanks to a significant increase in the signal to noise ratio. The probe current programme used for the analysis of dyes is reported in table 2.

Table 2: Probe current programme for the DE-MS analysis

Initial current	0 mA
Initial time	30 s
Ramp 1 rate	20 mA/s
Ramp 1 current	1000 mA
Ramp 1 hold	65 s

3 Analytical procedure

The analytical procedure, partially based on a previously published one [34, 35, 36], consists of:

1. Extraction of mordant dyes (flavonoids, anthraquinones and tannins) from the matrix: the samples were treated with 600 µL MeOH and 20 µL HCl (30%) at 65 °C for 60 min in ultrasonic bath.
2. Clean up: the extract is purified on a Nylon filter and dried under a soft stream of nitrogen (solution I).
3. Extraction of indigoid dyes: the residue of the extraction is further treated with 400 µL of DMSO (solution II).
4. DE-MS analysis: aliquots of 2 µL of solution I, reconstituted in methanol, and solution II are subjected to DE-MS analysis.
5. HPLC analysis: aliquots of 20 µL of solution I, reconstituted in acetonitrile / water mixture, and solution II were injected into HPLC system.
6. Derivatisation: 30 µL of the derivatisation agent BSTFA in 50 µL of AcOEt are added to a third aliquot of solution I in methanol; the reaction takes place at 70 °C for 30 min. Then, 5 µL of hexadecane (internal standard) and 150 µL of AcOEt are added.
7. GC-MS analysis: 2 µL of the final solution were injected into the chromatographic system.

4 Results

4.1 Red and pink shades

Figure 2 reports the HPLC chromatograms obtained for the analysis of red and pink samples. In sample I Ro1* and I Ro4 alizarin and purpurin were detected. Their presence was confirmed by GC-MS analysis (purpurin was detected in I Ro1* extract, while alizarin in I Ro4 one) and by DE-MS analysis: m/z 240 and 256 were clearly detected in both of the samples mass spectra. Gas chromatogram and mass spectrum obtained with DE-MS are shown in figure 3.

In sample I Ro1, I Ro3, I Ro5 carminic, kermesic and flavokermesic acids were detected by HPLC. These results could not be confirmed by GC-MS, being the molecular weight of target molecules too high to permit their separation and identification by this mean.

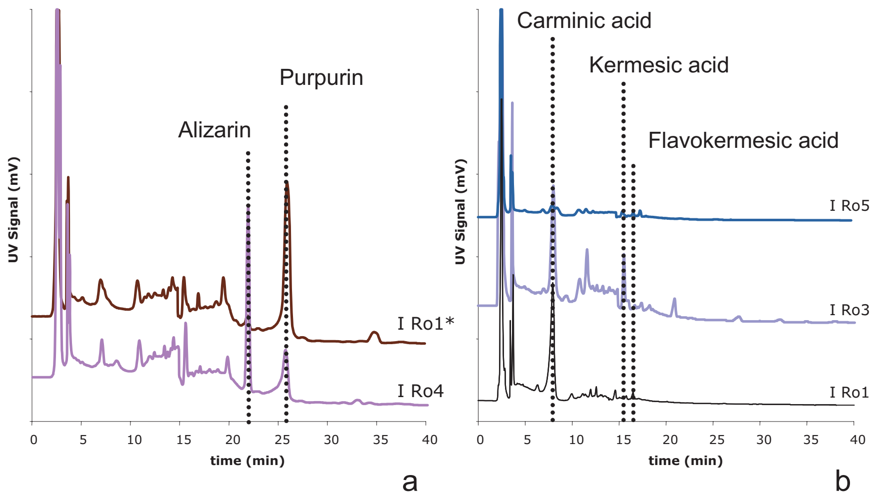

Figure 2: HPLC chromatograms of red samples: a) extracts containing madder lake molecular markers; b) extracts containing cochineal molecular markers

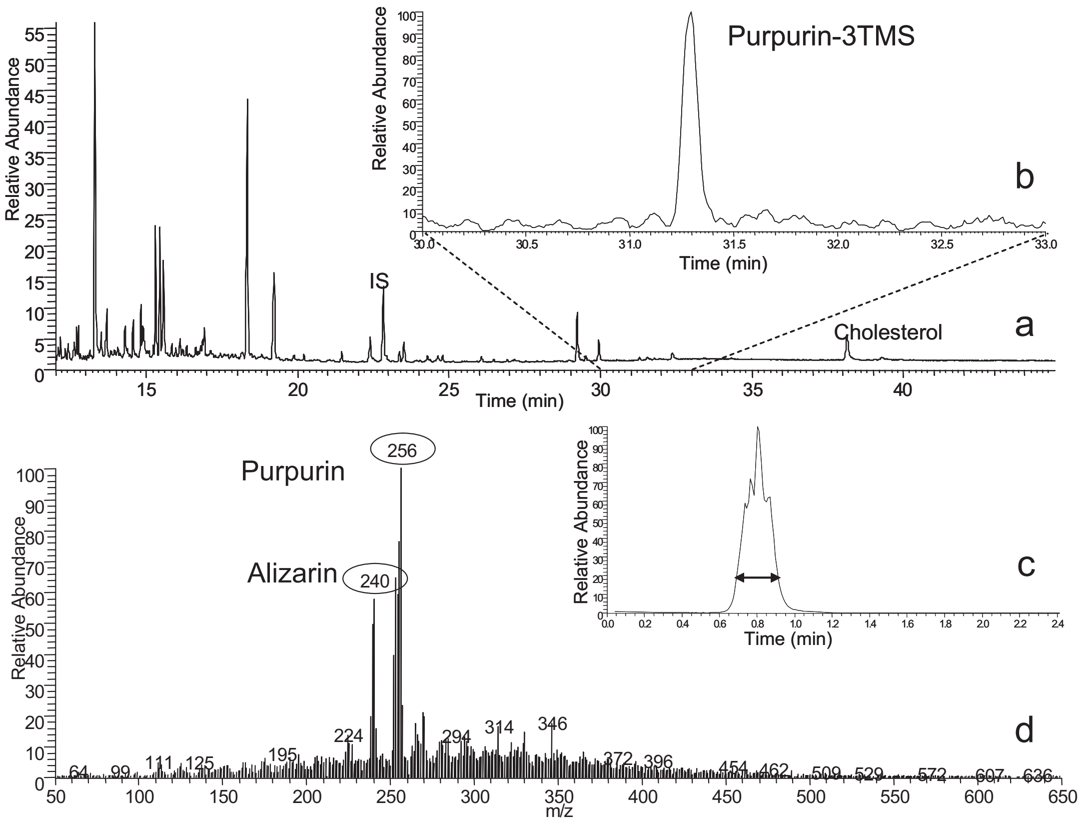

Figure 3: GC-MS and DE-MS analysis of sample I Ro1: a) total ion current chromatogram; b) extracted ion chromatogram (m/z extracted is 457, typical of purpurin-3TMS); c) total ion current chromatogram obtained with DE-S; d) average mass spectrum obtained with DE-MS*

Anthraquinoid dye source were identified by means of the three techniques in red and pink samples. Alizarin and purpurin, molecular markers of madder type dyes, were detected in two of the analysed samples; carminic acid, kermesic and flavokermesic ones were detected in the other samples, and their presence can be related to the use of cochineal (Polish or Armenian) dyestuff.

4.2 Yellow and green shades

Two yellow and one green samples were analysed. HPLC chromatograms permit to identify luteolin, apigenin and traces of kaempferol in sample I G1, as can be seen in the chromatogram in figure 4. In sample IV G1 some tannins and the flavonoid fisetin were identified. Both the identifications were confirmed by GC-MS analysis, while DE-MS did not give useful results. Gas chromatogram of sample IV G1 extract is shown in figure 5.

With regard to the green sample I Ve1, HPLC analysis suggested the presence of indigotine, and was confirmed by DE-MS; the yellow component of the green shade could not be identified by any of the three techniques.

The two yellow dyes were identified as flavonoid dyes: the presence of luteolin and apigenin suggest the use of weld; in the other sample's extract fisetin, molecular marker of Cotinus Coggygria, was identified: most probably sawwort's bark was used.

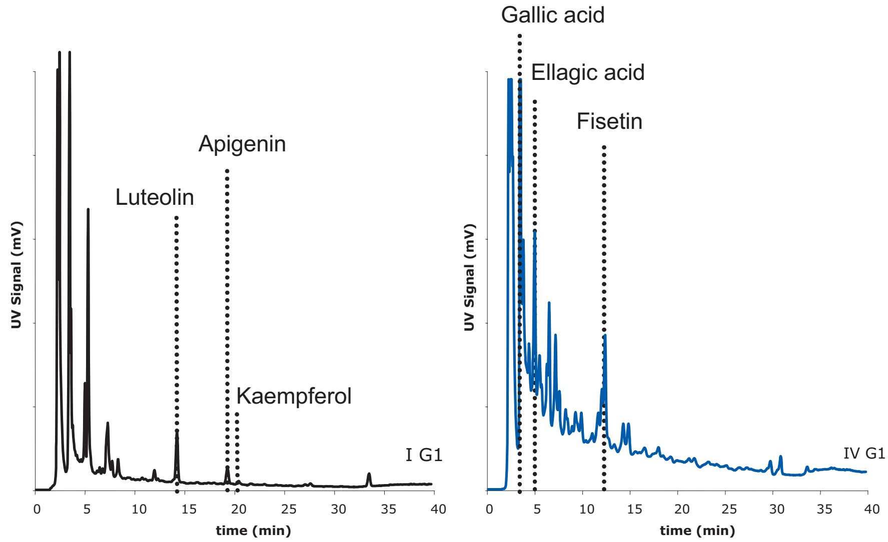

Figure 4: HPLC chromatograms of samples I G1 and IV G1

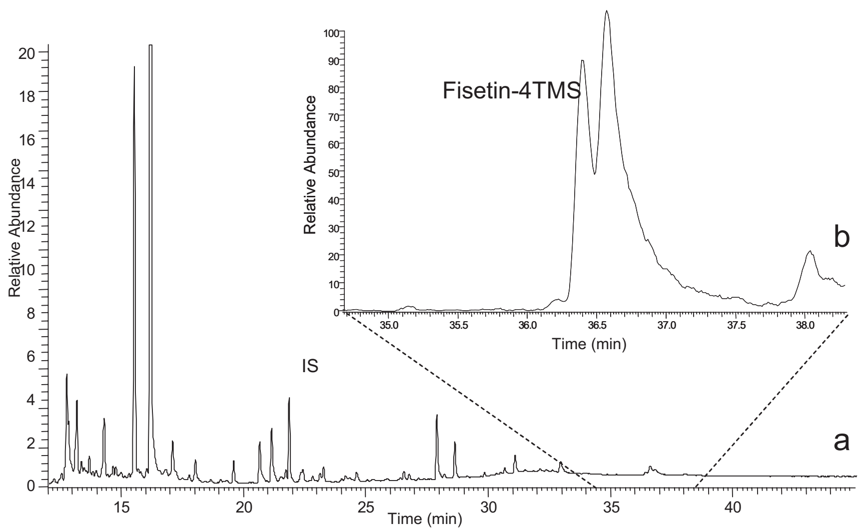

Figure 5: gas chromatogram of sample IV G1: a) total ion current chromatogram; b) extracted ion chromatogram (m/z extracted are 559 and 471, typical of fisetin-4TMS)

4.3 Black and brown shades

A brown and a black sample were analysed. The chromatographic profile (figure 6) obtained with HPLC analysis reveals the presence of a certain amount of very polar compounds, such as tannins; particularly, gallic and ellagic acid could be tentatively identified. GC-MS analysis permitted the unambiguous identification of gallic and ellagic acids in both of the samples. Moreover, in the second sample fisetin was determined thanks to the “extract ion” mode of data analysis.

In the first sample only gallic and ellagic acids were detected, suggesting the use of sumac or alder bark to obtain a black shade. The detection of fisetin, gallic and ellagic acids in the second sample suggests the use of a mixture of Cotinus Coggygria and tannins to obtain a brown colour. The use of young fustic leaves, which gives a much darker shade than the bark and contains an high amount of gallic acid, can not be excluded; in this case, ellagic acid presence may be due to a pre-treatment procedure for the silk thread, called weighting.

It should be underlined that the two dark threads show a high degree of degradation; this could be due to the corrosive action promoted by the presence of a ferric mordant plus a gallo-tannic dye.

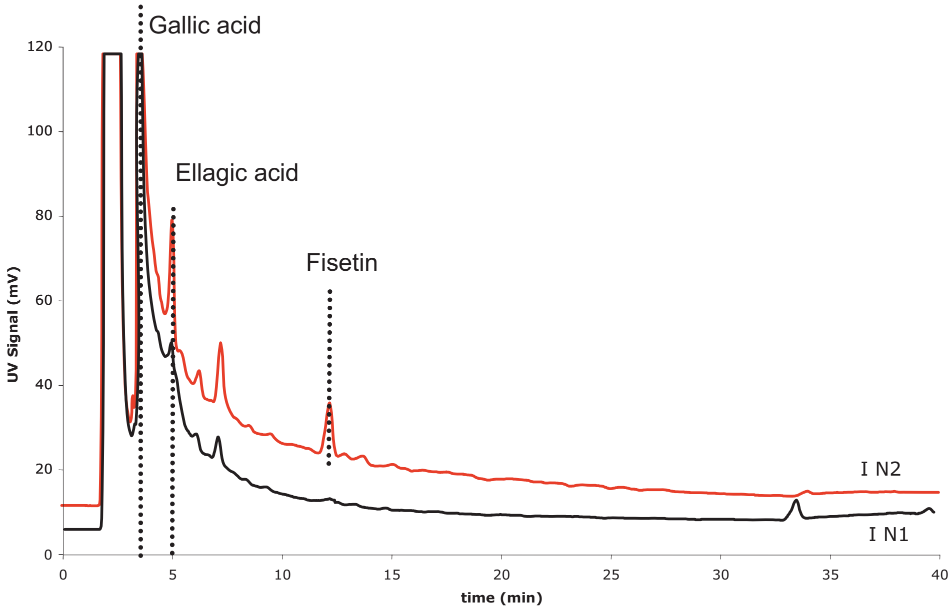

Figure 6: HPLC chromatogram of samples I N1 and I N2

5 Discussion

By the analysis of red, yellow and dark samples a wide range of dye sources was identified. Cochineal, madder, weld, young fustic and tannins were exploited to obtain different shades; the variety of colours available to the artist explains the richness of the artist's palette.
Identified dye sources are consistent with the tapestry dating, and the high quality of the materials is coherent with the high artistic value of the object.

Table 3: Sample list and molecular markers identified

Sample	Identified molecular markers	Hypothesis
I Ro1	carminic acid + kermesic acid	cochineal
I Ro1*	alizarin + purpurin	madder
I Ro3	carminic acid + kermesic acid + flavokermesic acid	cochineal
I Ro4	alizarin + purpurin	madder
I Ro5	carminic acid + kermesic acid + flavokermesic acid	cochineal
I G1	luteolin + apigenin + kaempferol	weld
IV G1	gallic acid + ellagic acid + fisetin	young fustic
I Ve1	gallic acid + indigotine	indigo + ?
I N1	gallic acid + ellagic acid	tannins
I N2	gallic acid + ellagic acid + fisetin	young fustic + tannins?

6 Conclusions

6.1 European dimension

The presented research contributes to the development of analytical procedures that permit the identification of artists' materials and techniques, thus giving interesting insights into European cultural roots. Particularly, the study of tapestries of different manufactures (Florentine and Flemish) gives us information on the availability and uses of dye sources in different areas of Europe.

6.2 Innovation and originality

The innovative aspect of this paper is the application of GC-MS method along with the classic HPLC-UV/Vis on the same microscopic sample, to the simultaneous identification of flavonoids, anthraquinones, tannins and indigoids in dyed wool and silk extracts. Particularly, in order to make flavonoids, anthraquinones and tannins detectable in complex mixtures by GC-MS analysis, a new procedure for the derivatisation of the analytes with N,O-Bis(trimethylsilyl)trifluoroacetamide was developed.

Moreover, a multianalytical approach was utilised: by means of three independent techniques, GC-MS, HPLC and DE-MS, stable molecular markers were identified in the extracts of historical samples, thus giving us reliable insights on the artist's palette.

6.3 Impacts

The possibility to identify the dye source in an old tapestry may considerably help not only in understanding how an object itself originally looked, but may also be a valuable tool in deciding how it should be cleaned and conserved. The proposed method allows the recognition of the dye source through the analysis of a very low amount of sample. This point is of paramount importance when analysing samples from Cultural Heritage.

It should be mentioned that nowadays there is an increasing demand for natural dye sources, due to the allergenic impact of some synthetic chromophores. The analysis of old textiles and therefore the unlocking of ancient technology could thus be interesting for industrial applications. Information on ancient dye sources and on the behaviour of natural chromophores with respect to natural ageing processes can help in drawing new routes for the modern dyes production.

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A methodology for the identification of organic materials in wall paintings

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Key words: binders, organic material, murals, wall paintings, non-invasive, invasive, Tintori

Abstract

To enhance the way science supports the conservation of wall paintings, the Getty Conservation Institute partnered with several European scientific laboratories to create the Organic Materials in Wall Painting (OMWP) project. This project was planned in two consecutive phases with the final goal to develop a methodological approach to facilitate the study of organic materials in wall paintings. The first phase is an evaluation of several investigation methods applicable to the identification of organic materials. The second phase is the application of the investigation methodology resulting from the first phase to case studies of wall painting undergoing conservation. For further information on the OMWP project the Getty Web site may be consulted at http://www.getty.edu/conservation/science/omwp/index.html.

In the first phase the project determined the efficiency and the limits of several investigation techniques applicable to the detection of organic materials in wall paintings using a set of wall paintings replicas of known composition made by wall painting conservator Leonetto Tintori. The method of evaluation was based on the level of information obtained and on the accuracy of the information provided. The following four levels of information were defined for the project:

Level 1: Presence of organic materials
Level 2: Class of organic material (e.g. proteins, lipids)
Level 3: Type of organic material (e.g. for proteins: egg, rabbit skin glue or casein)
Level 4: Organic materials in mixtures (e.g. drying oil and glue)

At each level, accuracy was measured by the percentage of correct identifications of the binders (or mixtures thereof) contained in the replicas.

Non-invasive techniques that do not require sampling of the paint layer reach only level 1 of information (i.e. they can detect the presence of organic material but not the class or type). Occasionally, non-invasive fibre optic infrared reflectance spectroscopy allowed identifying proteins or lipids (level 2). The analysis of cross-sections of the paintings (obviously an invasive technique) was hampered by the presence of the synthetic resins used to impregnate the sample and its usefulness could not be evaluated. Chromatographic techniques applied to the samples reached the highest level of information with high (but still not 100%) accuracy. A first test of immunologic techniques for protein identification yielded very promising results.

When these results are considered with respect to the actual study of real mural paintings, non invasive techniques appear to play an important role as they allow a general survey and the first detection and localization of the analytical problems without inflicting any damage to the paint layers. The experiments, however, revealed that the most popular non-invasive technique, detection of UV-induce visible fluorescence, may frequently fail (60% accuracy n the replicas studies) because of the interference of some inorganic material (e.g. red and yellow pigments). Therefore, the results of UV surveys of paintings should always be evaluated with great caution.

On the whole the results of the first phase of the OMWP project support the view that the best approach to the scientific investigation of wall paintings is through a stepwise passage from non-invasive to invasive techniques that allows a rational evaluation of results at each step to be conducted in close collaboration with the conservator in charge of the restoration. This paper illustrates the first phase of the OMWP project providing a general summary of its results.

1 Introduction

Understanding the original painting materials and its deterioration is necessary to ensure appropriate conservation procedures. When we deal with wall paintings we often hear the term *frescoes* to generally indicate a painting on a wall. This term, *a fresco* or *frescoes*, should be used to describe a very special way to paint that is exclusively limited to pigments applied on lime-based plasters before their setting and is restricted to a specific period of time and region of the world. Artists of all periods have used mixed painting techniques to decorate walls and have rarely painted purely *a fresco*. This misconception has resulted in inappropriate treatments causing for example the lost of portions of wall paintings which were painted 'a secco', i.e, applying pigments mixed with a binder after setting of the plaster.

Advanced methods of investigation available today have demonstrated that organic materials were used in wall paintings far more frequently than was thought in the past. Their identification is an essential part of all conservation projects in order to minimize the risk of damage and to improve the methods of intervention.

As part of a conservation project, understanding the presence of organic material is important for several factors including:

- Diagnostic investigation: understanding the causes and the processes of deterioration.
- Remedial conservation treatment: choice of methods that are compatible with the original materials.
- Risk assessment: understanding potential risks and adopt preventive conservation and maintenance methods.
- Art history: improve the knowledge of painting methods and materials.

Each conservation intervention is an opportunity to improve our understanding of methods and materials used by artists. It is important however to keep in mind that often this becomes the predominant aim of scientific investigation to the detriment of the other objectives.

Today there are several options and tools for investigations. There is not a single technique that can provide all the information we need and often we are left with the difficult task to decide how to address investigation issues in the best way. Frequently the investigations that we carry out are selected on the basis of what equipment is available rather than what would be the most appropriate method. This is not objectionable in line of principle but the limits of each analytical procedure must be well understood and the analyst must learn to work in close contact with the conservators in order to gain the maximum impact of the costly and time – consuming scientific investigations on the historic knowledge and the conservation process.

All these concepts are true in general for conservation of cultural heritage. When we deal specifically with wall paintings, the situation becomes even more complex due to the often vast painted surface that is examined and the tight conservation schedule that often provides no time for preliminary examination.

2 The OMWP project

In an attempt to improve the present methods of scientific investigation of mural paintings, the Getty Conservation Institute partnered with several European institutions to create the Organic Materials in Wall Painting project (OMWP) which started in 2003 and was developed in two consecutive phases. The first phase was devoted to the evaluation of the investigation methods presently used for the identification of organic materials and to the development of an investigation protocol. In the second phase, started in 2005, the most promising analytical techniques are applied to real case studies of wall painting undergoing conservation.

The analytical techniques evaluated in the first phase can be classified as follows according to their impact on the work-of-art:

- *non-invasive* (not requiring sampling);
- *invasive* (requiring sampling) – these can be further divided in:
  - *invasive non-destructive* (that allows further testing on the sample taken);
  - *invasive destructive (that completely destroys the sample).*

The partners that were involved in the first phase of the project – the evaluation of investigation methods for the identification of organic materials in wall paintings – are listed in table 1 together with the analytical techniques that they submitted to the evaluation process. Today a wide range of techniques is available for organic materials identification and there are other methods that might be applicable but have not been included in the present project.

Table 1: List of the investigations evaluated in the OMWP project first phase and corresponding research institutions and researchers involved

Non-invasive investigations	**Research group [researchers]**
Ultraviolet induced fluorescence photography	Opificio delle Pietre Dure, Firenze (OPD) [A. Aldrovandi, A. Keller]
Fluorescence life time and spectroscopy	Politecnico di Milano (PM) [D. Comelli, G. Valentini]; Consiglio Nazionale delle Ricerche (CNR) – Istituto per la Conservazione e Valorizzazione dei Beni Culturali, Milano e Firenze (ICVBC) [L. Toniolo, M. Matteini]; Università di Perugia (UniPG) [A. Romani, C. Clementi]; Getty Conservation Institute, Los Angeles (GCI) [G. Verri]
Imaging fluorescence spectroscopy	University of California at Los Angeles, Department of Material Science [I. Kakoulli]; GCI [L. Wong, G. Verri]; CNR – Istituto di Fisica Applicata Nello Carrara, Firenze (IFAC) [A. Casini]
Visible and mid-infrared reflectance spectroscopy	CNR – IFAC [A. Casini, M. Picollo]; GCI [G. Verri]
Infra-red reflectance spectroscopy	CNR – Istituto di Scienze e Tecnologie Molecolari, Perugia (CNR – ISTM) [C. Miliani]; UniPG [F. Rosi]; GCI [Verri]
Invasive investigations	**Research group [researchers]**
Cross-section preparation and examination in visible and UV light and stain tests	Courtauld Institute of Art, Londra (CIA) [A. Nevin, C. Martin de Fonjaudran]; OPD [G. Lanterna, C. Lalli]; Istituto Centrale per il Restauro, Roma (ICR) [F. Talarico, I. Giardina]
Infra-red reflectance spectroscopy on cross sections	CIA [A. Nevin]

μ-Infrared spectroscopy	CNR-Istituto di Chimica Inorganica delle Superfici, Padova (ICIS) [S. Vigato, E. Fiorin]; CNR-ISTM [C. Miliani]; UniPG [F. Rosi]; GCI [G. Verri]
Liquid chromatography	Laboratorio Scientifico dei Musei Vaticani [U. Santamaria, F. Morresi]
Gas-chromatography mass-spectrometry	University of Pisa (UniPI) [P. Colombini, G. Gautier]; University of Parma (UniPR) [A. Casoli, E. Campani]; GCI [M. Schilling, J. Mazurek]
Enzyme-linked Immunosorbent Assay for protein identification	GCI [J. Mazurek, G. Chiari], Getty Museum [A. Heginbotham], University of Southern California, Los Angeles [M. Quick]

The evaluation of the analytical techniques was carried out testing a series of 22 wall painting replica samples made by the late Leonetto Tintori and archived at the Tintori Center in Prato, Italy. The Tintori replicas are painted over one or two layers of lime-based plaster applied over terracotta tiles. Each replica is divided in sectors painted in a different way (see Fig. 1). Each sector is considered uniformly painted. The properties of the paint layer (a mixture of pigment and binder) are essentially conditioned by three variables: the phase of application (i.e. the timing of the application relative to the setting of the plaster), the type of pigment, and the type of binder. The phase of application corresponds to the level of carbonation of the plaster. The paints were applied on the plaster at different intervals after its application (from 2 hrs to a few days) providing several situation from fresh plaster (almost not carbonated) to set plaster (extensively carbonated). Types of pigments used included both pigments suitable for application on fresh plaster (such as earths and ochres) and unsuitable ones such as copper-based pigments and lead white. Two organic pigments were also included: madder lake and indigo. The binders used to make the replicas were: rabbit skin glue, casein, whole egg, walnut oil, linseed oil, and gum Arabic. All replicas are accompanied by a report describing their making and most of those selected for the OMWP project also are provided with quantitative information on the relative proportion of binder and pigment in the paint layer.

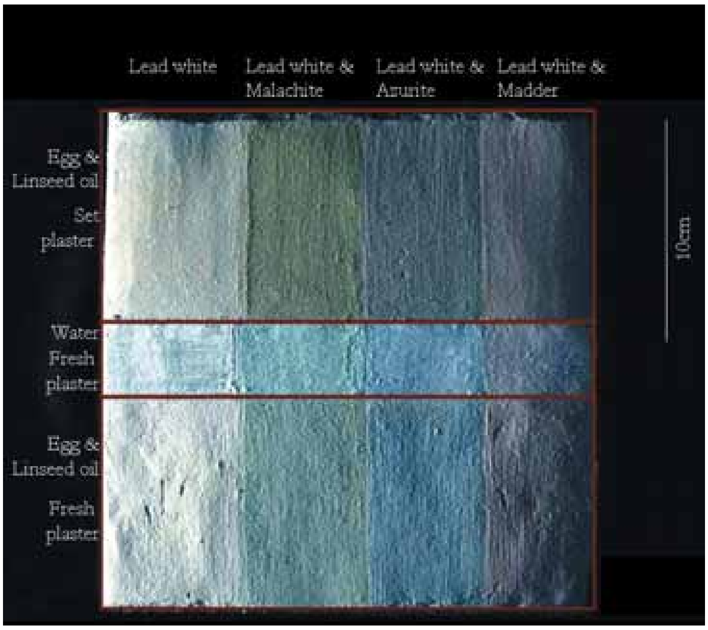

Figure 1: Example of one of the wall painting replica studied. The replica is divided in sectors – for a total of 12 sectors – The sectors in one column have been painted with the same pigment mixture. Sectors in one row have the same phase of application and the same binder.

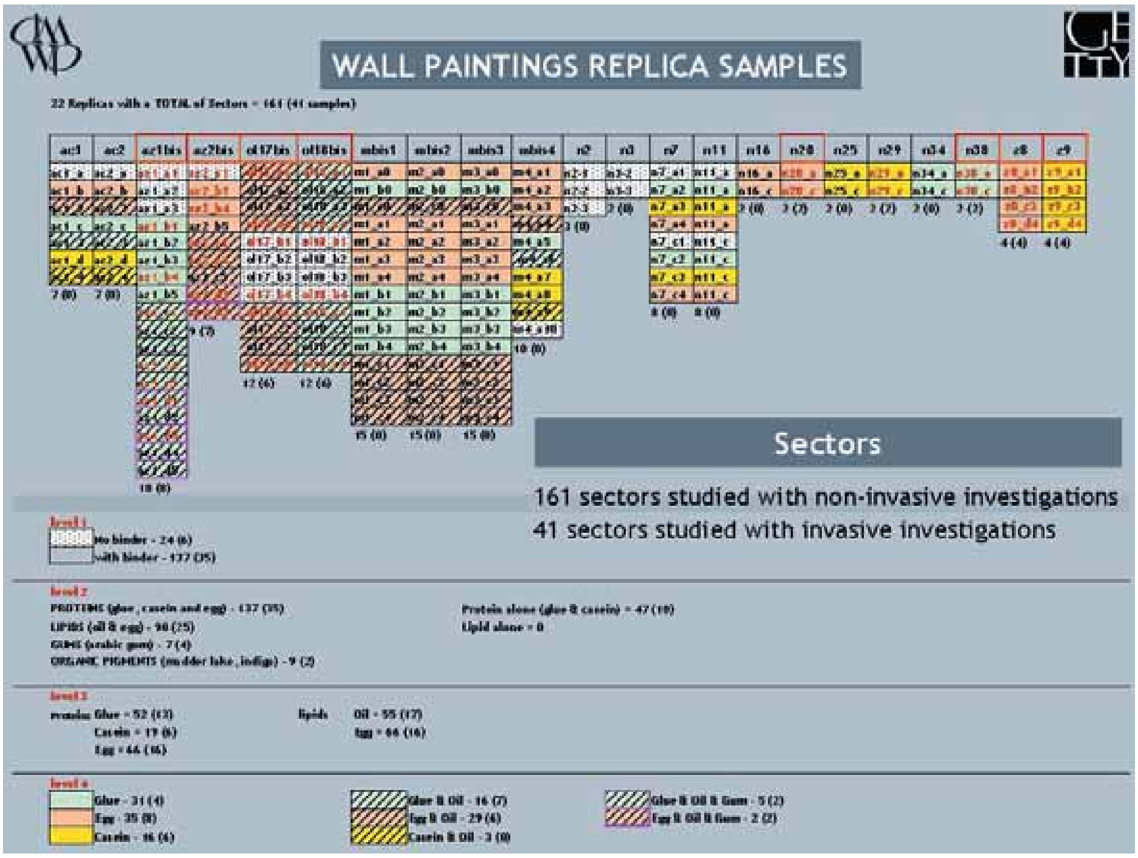

Figure 2: List of the sectors studied with indication of the organic material used. All the 161 sectors were studied with non invasive techniques and of these, 41 were also studied with invasive methods

3 Evaluation of analytical techniques

The objective of the first phase of the OMWP project was the evaluation of the ability of each individual technique to detect organic materials in the set of wall paintings replicas tested. The evaluation of the techniques is based on the level of information obtained (sensibility) and the correlation factor (accuracy) for the type of information searched. Four levels of information defined for the OMWP project as follows:

Level 1.
Presence of organic materials

Level 2.
Class of organic material. The classes tested include:
proteins, lipids, gums, and organic pigments

Level 3.
Type of organic material. The types tested include:
proteins: rabbit skin glue, casein and whole egg
lipids: linseed oil or walnut oil and whole egg
gums: gum Arabic
organic pigments: madder lake and indigo

Level 4.
Organic materials in mixtures. The mixtures tested include:

linseed or walnut oil and glue
linseed or walnut oil and whole egg
walnut oil and whole egg and gum Arabic
walnut oil and glue and gum Arabic

When possible, a correlation factor has been calculated for the set of sectors studied and for the level of information obtained and is expressed as % of Positive, % Uncertain, and % Negative correlations to the data on the original composition of the paint layer recorded in the relevant production report.

Positive correlation: the output of the technique corresponds to the recorded composition of the sector in the replica

Uncertain correlation: the output of the technique is uncertain with respect to the composition of the sector

Negative correlation; the output of the technique does not correspond to the composition of the sector

The correlation factor represents the capability of each individual technique to characterize the organic material in the replicas under investigation. The correlation factor is calculated for four levels of information defined for the OMWP project as follows:

3.1 Results

In May 2006 the results from the first phase of the Organic Materials in Wall Paintings (OMWP) project were presented at a day-long symposium held at the Centro di Conservazione e Restauro La Venaria Reale near Turin, Italy. In attendance was a diverse group of experts from the field of wall paintings conservation including art historians, architects, conservators, and conservation scientists. At the symposium, each of the OMWP partner teams illustrated results from their method of analysis and the extent of the method's ability to detect organic materials in the wall paintings replicas tested. The results are extensive and will be published as part of the OMWP project. An overview of the results will be provided here underlining the most important ones.

The first comment to be made is that the evaluation of the results has been done on a limited and specific set of samples both in terms of amount and type of material tested. Obviously, the real situation, on wall paintings affected by centuries of exposure, contamination and deterioration factors makes the whole situation much more complex. The evaluation of the investigations is based on the level of information obtained and on the correlation factor for that level. While the level of information obtained is a function of the technique, the correlation factor, due to its statistical nature, is strongly affected by the set of samples tested and should be considered with caution for general application (see Figure 2 for the statistical distribution of materials in the sectors studied).

3.1.1 Non-invasive investigations

This kind of investigations is very important when studying the vast and heterogeneous surfaces of wall paintings. Investigation methods are in constant evolution as laboratory equipment becomes portable and suitable for in situ examination. Non-invasive in situ examination provides the opportunity to obtain results on the nature of materials on site without the removal of samples. One advantage is the possibility for the scientist to work in close contact with the conservators who should be able to transfer to him their understanding of the painting techniques based on visual examination and their accumulated experience.

Several of the non-invasive methods tested are based on ultraviolet induced visible fluorescence and include: imaging, spectroscopy and life time. All of these UV fluorescence based methods allow determining the presence of fluorescent material and are, of course, limited to the surface of the paintings. The emission band of all organic materials tested in the OMWP project is centred in the region of 440 nm and it is therefore not possible to distinguish the class of organic material. It is possible however, to distinguish between organic binders and organic pigments with fluorescence spectroscopy. This distinction is not possible with imaging techniques.

Essentially UV fluorescence-based methods provide information at the level 1. It is important however, to report that the accuracy of the results is rather low providing, for example in the case of UV fluorescence photography, around 60% of positive correlation and 40% of negative correlation. This is due to chemical-physical interaction between the fluorescence emission and the materials in the paint layer through phenomena such as quenching and light absorption which may cause false negative results especially in the presence of red and yellow pigments (note: this topic and the development of method for improving imaging of UV fluorescence are the subject of additional investigation currently undertaken by Giovanni Verri). In other words, the presence of fluorescence is always linked to the presence of a fluorophore while the absence of fluorescence not always corresponds with the absence of a fluorophore. Obviously this may be a quite dangerous error when the study of a painting is limited to the study of UV fluorescence in order to determine if some parts were painted with a binder (*a secco*).

Often fluorescent material in a wall painting is organic, either included in the original paint layer or added during restoration programs, such as natural or synthetic binders, organic pigments and varnishes. There are, however, examples of inorganic fluorescent materials (e.g., zinc white and some soluble salts). Also calcite (calcium carbonate) may be fluorescent if defects (e.g. impurities) are present in its crystal structure. It is therefore essential to correlate the presence of fluorescence with the nature and distribution of pigments and contaminants present, and so the knowledge of inorganic materials present in the paintings is important to properly interpret results obtained from investigations based on UV fluorescence both to identify possible false negative results and to be able to attribute correctly the fluorescence to organic materials present in the paint layer.

Among non-invasive techniques of instrumental analysis evaluated in the project, in situ fibre optic infrared reflectance spectroscopy appears to be the most successful and innovative. This technique proved to be very accurate for level 1 providing a very high correlation factor for the 161 paint compositions examined (almost 100% positive correlation). Furthermore this technique was the only non-invasive one which was able to provide some information at level 2 (i.e. determine if the organic material identified is a protein or a lipid). The accuracy obtained for level 2 was approximately 70% for lipids and 80% for proteins for the set of samples tested.

3.1.2 Invasive investigations

Invasive investigations may be carried out either directly on cross-sections of a painting or on individual layers of paint separated from the rest of the structure in the sampling process or under the microscope. Cross-sections are very important as they allow determining the stratigraphy of the work that is being studied.

The identification of organic materials in cross-sections can be done with various methods (see table 2). However, most of these methods were jeopardized by the presence of the organic resins (typically poly-ester or epoxy resin) used to embed the sample and smeared over the cross-section during cross-section polishing. This problem was addressed as part of the OMWP project with an evaluation of alternative sample preparation procedures which provide promising but not entirely satisfactory results (and therefore require further research). The interference of the embedding resin is particularly evident with wall painting samples due to the porosity of the paint layer which allows the resin to impregnate completely the material. For this reason all methods of analysis did not yield good results (in all cases organic material was identified either due to the sample or to the resins used or to both of these factors). Therefore the correlation factor was not calculated for these methods and the evaluation was limited to determine the level of information that could have been reached.

Many organic materials exhibit fluorescent properties in the visible region when excited by UV radiation. Direct observation of fluorescence may be indicative of the presence of organic materials (level 1), but it is not sufficient to give precise information on their nature. The same problems described for non-invasive methods based on UV fluorescence, such as quenching of the fluorescence and the occurrence of false negative responses, occur when examining a cross-section in UV light. Stain tests on cross-sections using coloured and/or fluorescent dyes may indicate the presence of broad classes of organic materials (proteins, lipids or gums) reaching therefore level 2. However, the interference with the embedding resins and the difficulties in interpretation especially for the highly porous wall painting samples makes this type of investigations difficult and not quite reliable.

Invasive destructive investigations on fractions of the sample taken from the replicas provided the highest level of information and the best correlation. Micro-FTIR methods are very efficient for the identification of the presence of organic material and for the characterization of the class (Level 1 and 2). Micro-FTIR on untreated portion of a sample resulted in a better correlation factor when compared with the same method applied on solvent extracts (using water for the extraction of proteins and chloroform for the extraction of lipids). The difference seems to be mainly associated with difficulties in the extraction of the organic materials from the paint layer and in the handling of the sample. In addition extraction procedures require a much longer time for the analysis.

Finally, gas-chromatography methods appear to be the only ones capable of providing information up to level 4 (characterization of mixture of organic binders). A notable exception however is the case of mixtures of egg and oils that cannot be fully characterized due to the lipid content of the yolk.

The innovative use of Enzyme-linked Immunosorbent Assay (ELISA) for the extremely specific characterization of proteins proved very successful for the samples tested with almost 100% correlation rate at level 4 for the proteins mixtures. Antibodies can only distinguish between different types of proteins. The integration of results of GC-MS and ELISA allows for the characterization of oil and egg mixtures.

Invasive investigations appear to be necessary to provide a higher level of information but they require sampling. Sampling is by far the highest source of error in analysis because the separation of the original paint layer from all types of contamination is not easy and the sample must be representative of the problem studied. Furthermore the result is valid for a single point and not many of them can be sampled.

Non-invasive investigations, on the other side, do not provide high level of information or accuracy but they do cover the entire surface of the painting and, if their limitations are well understood, they are essential in the development of an appropriate strategy for representative sampling and invasive investigation.

4 Conclusions

Appropriate conservation treatment of wall paintings should be minimal, compatible with the original material, and stable in the long term. To achieve this, interventions – both preventive and remedial – must be developed according to a methodology that begins with the characterization of the material constitution of the paintings through rigorous diagnostic investigations.

The goal of the OMWP project is to enhance the ways in which science supports the conservation of wall paintings by developing a set of guidelines to facilitate the investigation and characterization of organic materials present in paint layers that are most susceptible to damage in the course of restoration projects.

While the identification of inorganic components in wall paintings today is a relatively straightforward process, doing the same for organic materials remains a challenge. The difficulty arises principally from four factors:

1. the low binder-to-pigment (and other inorganic materials) ratio;
2. the unstable chemical-physical nature of organic materials, which may result in rapid and dramatic decay;
3. the large, often vast, heterogeneous, open and porous wall painting systems, which are highly susceptible to degradation and contamination;
4. the complex interactions among the painting materials (typically pigments and binders but also other materials), which can limit and alter the capability of scientific instruments to identify organic materials.

There is not a single area of expertise or a single investigative technique that can be used to efficiently detect organic materials in wall paintings. Different types of investigations and techniques must be used and integrated to obtain significant results. Characterizing organic materials through scientific investigation in a way that is both resource effective and that minimizes the amount of sampling required has been a principal aim of the OMWP project.

The conclusions we can draw at the present state of our knowledge is that the best way to study compositions of paint layers is through a sequence of non-invasive and invasive investigations; an iterative diagnostic process which requires on site data evaluation and interpretation by the scientist in collaboration with the conservators in charge and a consequent reconsideration of the investigation strategy at every step.

5 References

A list of literature reference for the OMWP project is available at:
http://www.getty.edu/conservation/science/omwp/ omwp_publications.html .

An early warning system for organic materials in museums, historic buildings and archives

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Key words: dosimeters, early warning, organic objects, museums, preventive conservation

1 Introduction

All over Europe objects in museums, historic buildings and archives are being affected by environmental conditions. Unsuitable environmental conditions are a serious cause of deterioration, frequently made worse because the effects may remain invisible for a long period. An Early Warning system for Organic materials (EWO system) has been developed as an important part of the EU funded project "Preventive Conservation Strategies for Protection of Organic Objects in Museums, Historic Buildings and Archives" (MASTER), (EVK4-CT-2002-00093). The aim of the MASTER project was to provide museums, historic buildings and archives with a new and refined preventive conservation strategy for organic objects based on an EWO system that can identify environments where damage to collections is likely [1].

Preventive conservation started to be recognised as a distinct branch of conservation after the publication of the important work by Garry Thomson in "*The Museum Environment*" [2]. Most preventive conservation strategies have been created for mixed material collections. An example is Keene's mixed collection survey [3]. Furthermore, preventive conservation strategies are often integrated with other conservation practices and museum activities [4]. These were important considerations for the development of the Early Warning system for organic objects in the MASTER project. The group of "organic objects" includes materials with very different properties. Organic materials are very complex in structure and their deterioration is a complex field with a broad range of different chemical reactions. The most prominent reactions are thermally or photo-chemically induced oxidation process and ionic hydrolysis reactions caused by acids or other catalysts [5]. Reactions caused by Ultra Violet (UV) and by visible light are also very important processes. However, the importance of relative humidity (RH), temperature and air pollutants such as O_3, NO_2 or SO_2 should not be underestimated. All the reactions will create changes in the organic structure caused by changes in the chemical bonding and may lead to deterioration that prevents heritage objects' use.

For a long time there has been a need for an acceptable general technology for early warning of environmental risk to organic objects collections, and for a new preventive conservation strategy that include all the relevant information affecting object preservation. This is particularly important for organic objects that are often present in large numbers in collections such as those of historic buildings with original textile furnishings and decorations; or in libraries and archives, which hold large numbers of paper documents.

The EWO system developed in the MASTER project consists of dosimeters based on two different principles and a new preventive conservation strategy. A particular important feature of the dosimeters is that results can be measured at location with an affordable portable measurement instrument. Very important for end-users is the preventive conservation strategy developed by Centre for Sustainable Heritage at University College of London.

2 The early warning dosimeters

In the MASTER project two early warning dosimeters were developed. The EWO-Generic (EWO-G) dosimeter mainly developed by NILU, that responds to a wide range of environmental parameters as a generic, integrating device [6] and the EWO-Specific (EWO-S) dosimeter, mainly developed by ALU-FMF, that measure the doses of the separate gases NO_2, O_3 and SO_2 [7]. The technical and use characteristics of the two dosimeters are given in Table 2.1. The dosimeter chips were produced in the laboratories of ALU-FMF. The EWO dosimeters consist of a borosilicate glass carrier ($15 \times 7 \times 1$ mm³) surface coated with a thin polymer film using a spin coating technique.

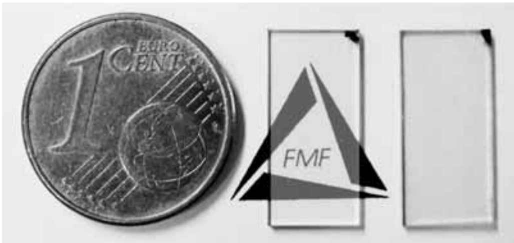

Figure 1: Two different dosimeters after the production, compared to a one-cent coin

The evenness and thickness of the polymer films and their permeability are important characteristics for their reactivity. The EWO-G polymer layer itself is vulnerable to photochemical and chemical processes induced by UV-light and chemical stress factors [8] that can simulate the degradation of organic materials. An indicator reagent, sensitive to a specific air pollutant, is immobilized into the polymer layer of each EWO-S dosimeter chip (Figure 1). The prototype of the final EWO-S dosimeter consists of an array with the three single dosimeters, for NO_2, O_3 and SO_2, fit in a holder with a light shield (Figure 3). The main principle of the EWO-S dosimeters is the irreversible change of the absorption spectra of the dosimeters in contact with the determining gas. Changes in the polymer [9], and polymer and dye, films are easily detectable by UV-visible spectroscopy. Portable measurement instruments for easy evaluation of environments in the field have been designed for the two dosimeters (Figures 2 and 3). The numeral result is shown in the displays as a light indicator corresponding to the aggressiveness of the environment and trigger levels presented in Chap. 5.

3 Laboratory exposures

3.1 The EWO-Generic dosimeter

The EWO-Generic dosimeters were exposed in a climate chamber at NILU to varying concentrations of the single and combined pollutant gases NO_2, O_3, SO_2 and CH_3COOH, under selected conditions of RH and temperature. A close to equal linear effect was observed for NO_2 and O_3, and for equal mixtures of NO_2 and O_3, in the range from 20 to 100 ppb at RH = 45 and 70 %, with some indication of a slightly higher effect for O_3 and at high humidity. The effect of SO_2 was only observed at the high RH = 70 %, at concentrations > 60 ppb, increasing to an effect slightly lower than that of NO_2 and O_3 at 100 ppb. No effect was observed for acetic acid at RH = 70 %. The final calibration of the EWO-G was performed by statistical analysis of the field test data (Chapter 5.1).

Table 1: Technical and use characteristics for the two different dosimeters developed in the MASTER project

	EWO Generic dosimeter	EWO Specific dosimeter
Technical characteristics:		
Environmental factors monitored	Generic effect of O_3, NO_2, SO_2[1)] Temp, (RH[2)]) and UV-light	Specific effect of O_3, NO_2 and SO_2
Technology – construction	The dosimeter chip is a polymer film (thickness ≈ 1.5 μm) spin coated on a glass substrate (15 × 7 × 1 mm)	The dosimeter chip is a polymer film mixed with a gas sensitive dye (thickness ≈ 1.5 μm) spin coated on a glass substrate (15 × 7 × 1 mm)
Technology – working principle	Environmental hazards degrade the polymer film. Bond breaking and cross-linking makes the film more opaque. The opaqueness is proportional to dose of degrading environmental influences. The dose measurement is correlated with doses known to degrade organic objects.	Gases reacts with single dyes mixed in separate polymer films. The reaction leads to a colour change of the film, which is proportional to doses of the gases. The dose measurements are correlated with doses known to degrade organic objects.
Recommended exposure time	3 months	1 month
Immediate measurement unit	Dose observed as change in light absorption in polymer film.	Dose observed as change in light absorption in dyed polymer film.
Derived measurement unit	Will only be available when all but one of the generic effects are known from other information	Mean concentrations of the three single gases
Measurement technology	Photo spectrometry	Photo spectrometry
Measurement options	Laboratory measurement or measurement on location with handheld single wavelength instrument.	Laboratory measurement or measurement on location with handheld single wavelengths instrument.
Use characteristics:		
Visible change	Yes (indirectly on handheld instrument)	Yes (indirectly on handheld instrument)
Ease of use	Simple operating procedure	Simple operating procedure
Ease of interpretation	Measurement needs comparison with acceptability chart	Measurement needs comparison with acceptability chart
Environmental impact	Inert – no impact	Inert – no impact
Size (indicating dimensions)	Holder: (8 × 2 × 0.3 cm) Portable measurement instrument: (15 × 8 × 6 cm)	Holder: (8 × 2 × 0.3 cm) Portable measurement instrument: (15 × 8 × 10 cm)
Durability /shelf-life	Good (months to years) in unopened package. Increased when kept cool.	Good (months to years) in unopened package. Increased when kept cool.
Short-long term options	Partly with dose measurement at intermediate times	Partly with dose measurement at intermediate times
Range of dosi-meter sensibilities	High to medium	High to medium
Can be related to other kinds of monitoring ?	Depends on environmental data available	Yes, directly.
Diagnostic use	Depends on environmental data available	Yes, directly.
Important environ-mental risks not monitored	Light and organic acids	All, except NO_2, O_3 and SO_2.

[1)] At RH > 60 %, [2)] Isoperm adjustment of temperature effect

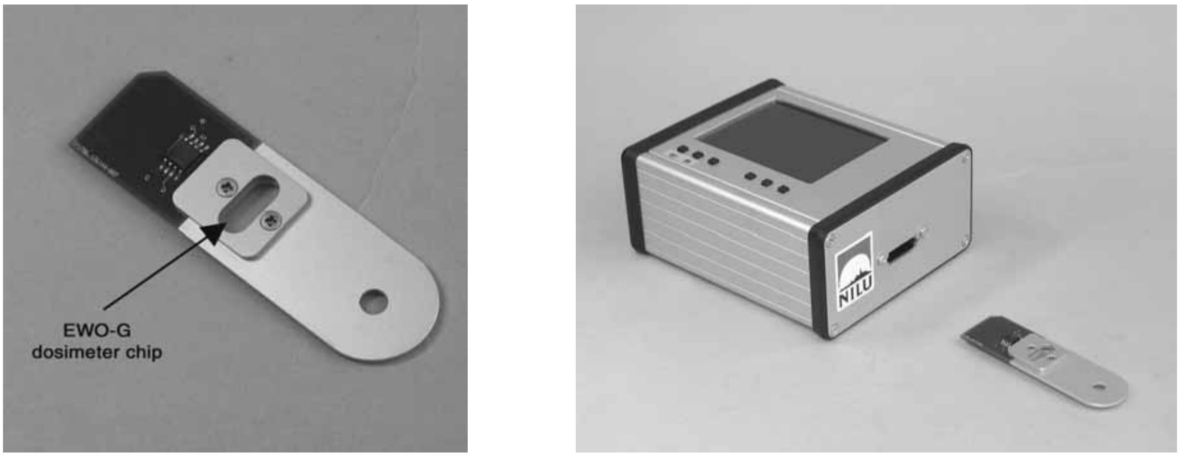

Figure 2: The prototype of the EWO-G dosimeter and holder (left) and its portable measurement instrument (right)

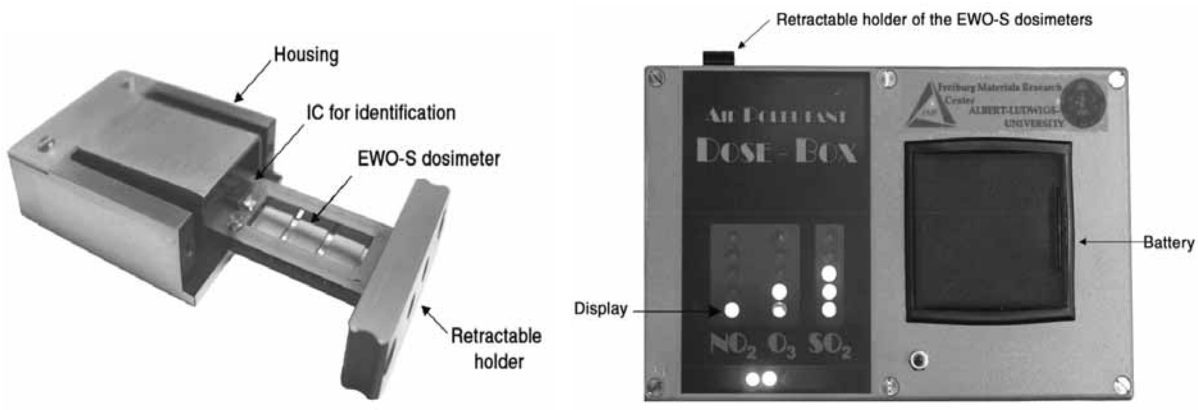

Figure 3: Prototype of the final EWO-S dosimeters, packed together as a single array (left) and of the portable measurement instrument (right)

3.2 The EWO-Specific dosimeter

The dosimeters were placed for several weeks in flow-through desiccators under gas concentrations expected for museums (0-100 ppb NO_2, 0-50 ppb O_3 (also mixed gases) and 0-10 ppb SO_2). The airflow, relative humidity and temperature (average = 23 ^oC) were measured. With few days intervals the dosimeters were temporarily taken from the desiccators for analysis in a spectrophotometer. Dosimeter requirements were that they should be passive and be exposed for several weeks. 60 different purchased and self-synthesised indicator reagents (antioxidants, redox indicators or amines for the determination of NO_2 and O_3 [10-17] and oxidants for determination of SO_2 [18-19]) were tested to find the most suitable reactive components. The change in absorption of the EWO-S dosimeters from before to after exposure, at a single wavelength higher than ≈ 380 nm, gives the information about the average gas concentration during exposure. The change in absorption was found to be directly proportional to the exposure time at a constant gas concentration according to the Lambert-Beer law [19]. Table 2 gives the specifications for the EWO-S dosimeters.

Table 2: Calibration properties of the EWO-Specific dosimeters

EWO-S dosimeter: Characteristics	NO_2	O_3	SO_2
Calibration equation[1)]	$c = 28112 \cdot \frac{\Delta A}{t}$	$c = -3642{,}7 \cdot \frac{\Delta A}{t}$	$c = -1217{,}7 \cdot \left(\frac{\Delta A}{t} + 3{,}06 \cdot 10^{-4}\ d^{-1}\right)$
Detection limit (DIN 32645) – Probablilty of error = 5 %, – Exposure time = 28 days	3.46 ppb	2.84 ppb (RH < 5%)	0.72 ppb (RH < 5%)
Upper limit of determination – Exposure time = 28 days	> 100 ppb per day	> 30 ppb per day	3 ppb per day
Interferences	O_3 (at concentrations higher than typical indoors)	NO_2 (6.2 ppb response at 100 ppb NO_2) RH (decreasing response with increasing RH)	RH (increasing response with increasing RH, Accelerated crystallization of indicator reagent at higher humidity)

[1)] The initial constant has the units ppb * days(d) and ΔA depends on time.

4 Field exposures

4.1 The content of the field test programme

The environmental effects on organic materials in museums, historic buildings and archives is mentioned in the literature [1, 5], but scarcely quantified. Results from questionnaires in the MASTER project showed that many European museums and historic buildings were unaware of the effects of certain risks, especially pollutants [21]. To establish an environmental database, for testing and calibrating the EWO dosimeters against the environmental parameters, and directly or indirectly against organic reference materials like paper and silk, an extensive field test was carried out during one year in 10 different museums and historic buildings from 5 different regions in Europe, each one including a rural and urban site (Table 3).

Table 3: Museums participating as exposure and monitoring locations in the MASTER project field test (u) = urban, (r) = rural

Name of museum / historic building	Location *, Country	Site number
The Museum of Decorative Arts & Design	Oslo, Norway (u)	1
Trøndelag Folk Museum	Trondheim, Norway (r)	2
Blickling Hall	Norfolk, UK (r)	3
Tower of London, Bloody Tower	London, UK (u)	4
Haus der Geschichte Baden-Württemberg	Stuttgart, Germany (u)	5
Schwarzwälder Trachtenmuseum	Haslach, Germany (r)	6
National Museum in Krakow, The Jan Matejko House	Krakow, Poland (u)	7
The Karol Szymanowski Museum "Atma"	Zakopane, Poland (r)	8
Wignacourt Collegiate Museum	Rabat, Malta (u/r)	9
The Historical Museum of Crete	Heraklion, Crete (u)	10

*Only name of location will be used in the graphs presenting the monitoring results.

The field test was performed with separate exposures outdoors (A), indoors in the exhibition area (B) and inside showcases (C). In all three locations parallel samples of the EWO-G and EWO-S dosimeters and passive gas samplers (O_3, NO_2, and SO_2, and organic acids in location C) and single samples of organic objects; paper, silk and blue wool light dosimeters, were placed on a similar specifically designed exposure rack. Measurement instruments and loggers for the climatic parameters (T, RH and Light) were placed on the same location. The EWO-G dosimeters were exposed shielded from light and fully exposed to the light. The EWO-S dosimeters were only exposed shielded from light. One, three and six months samples were exposed for the EWO-G. Monthly samples were exposed for the EWO-S. The passive gas samplers were exposed for 1 month, the blue wool dosimeters, silk and paper samples were exposed for one year. Temperature and relative humidity were monitored and logged continuously for locations B and C. Mean monthly values were calculated. For location A, monthly average data from local meteorological stations were reported. Light (lux) and UV (mW m^{-2}) were measured in locations B and C at 12 o'clock noon as a single spot measurement and were monitored continuously for periods in some sites with less stable lighting conditions. Mean yearly values were reported. Analysis of passive gas samplers and dosimeters were performed in the laboratory at NILU. All project data were collected in a database at NILU to be used in the evaluation of the dosimeters.

4.2 Results from field testing of the EWO-G dosimeter

The EWO-G dosimeter was exposed unshielded for 3 months, as the effect is relatively linear with time up to 3 months, with some saturation only reached for the most exposed sites. Figure 4 shows the mean 3 months response of the EWO-G unshielded dosimeters for the A (outdoors), B (indoors, exhibition area) and C (showcase) locations at the 10 sites.

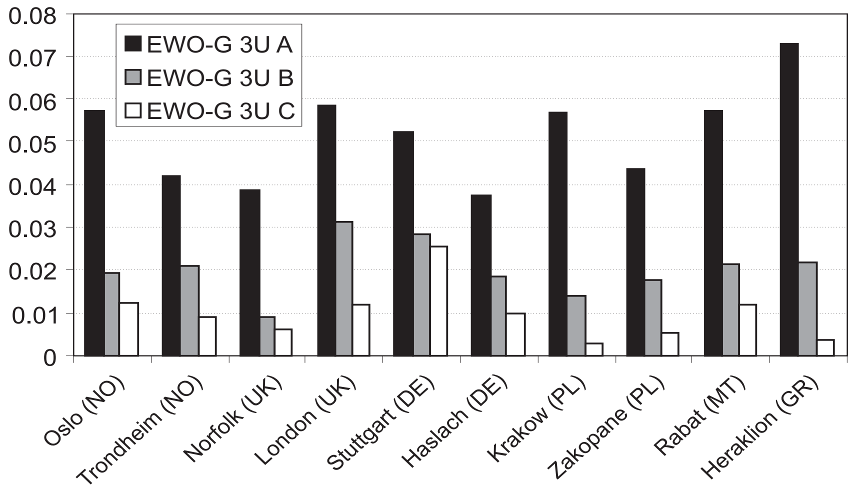

Figure 4: Mean response of four 3 months exposures for the EWO-G unshielded dosimeters on the A (outdoors), B (exhibition area) and C (showcase) locations at the 10 museum test sites

4.3 Results from field testing of the EWO-S dosimeters

The EWO-S dosimeters for NO_2, O_3 and SO_2 were exposed in the field test during selected months to evaluate responses in "real" exposures outside the controlled laboratory setting. Figure 5 shows a correlation of EWO-S dosimeter and NO_2 passive sampler results.

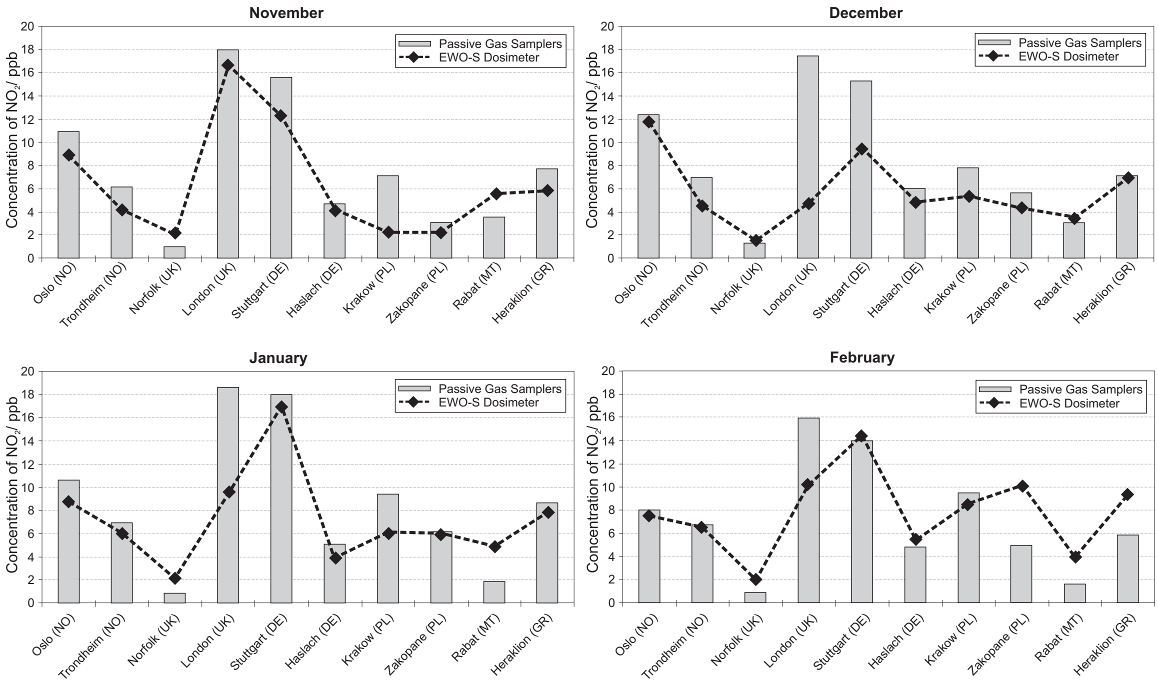

Figure 5: Comparison between the results of the passive gas samplers for NO_2 – blue bars – and the results of the EWO-S dosimeter sensitive for NO_2 – red rhombus – at all exposure sites from November 2004 till February 2005

5 Calibration and threshold values

5.1 Correlation of environmental measurements and the dosimeter effect

Mean 3 monthly values for the environmental parameter measurements and EWO-G dosimeter response values were correlated using multivariate regression analysis. This analysis gave the calibration equation, with uncertainties (95 % level, two sided) in brackets [22]:

$$\text{EWO - G effect (x1000)} = 0.75(0.17)\text{NO}_2 + 1.34(0.3)\text{O}_3 + 0.51(0.088)\text{T} + 0.35(0.21)\text{UV}$$

with NO_2 and O_3 (ppb), T (^{o}C) and UV (mW m^{-2}). Table 4 gives the calibration intervals and statistical detection limits for the EWO-G under average conditions for the field test.

Table 4: Statistical detection limits for the EWO-G under average conditions for the field test

Independent variable	Calibration interval	Control variables – mean values in museums	Detection limits (ppb)
NO_2 (ppb)	1-20	O_3 = 5.0 ppb, UV = 4 mW m^{-3}, T = 19.7 ^{o}C	3.3
O_3 (ppb)	0.5-30	NO_2 = 7.7 ppb, UV = 4 mW m^{-3}. units, T = 19.7 ^{o}C	1.7
T (^{o}C)	10-30	NO_2 = 7.7 ppb, O_3 = 5.0 ppb, UV = 4 mWm^{-3}	4.2
UV (mW/m^2)	0-15	NO_2 = 7.7 ppb, O_3 = 5.0 ppb, T = 19.7 ^{o}C	7.5

The laboratory calibration of the EWO-S is described in Chapter 3.2.

5.2 Assessing the museum environments with the EWO-G dosimeters

Assessment of museum environments with the EWO-G dosimeter is based on the calibration equation (Section 5.1). The dosimeter result-effect of exposure is given as one number value, representing the change in UV absorption from before to after exposure. The effect is related to measures of effects reported on organic materials for single or combined environmental parameters. Literature data for effects observed for NO_2, O_3, UV-radiation and temperature were used [23, 24, 1]. The temperature values were set for RH values of 45 %, 55 % and 65 %, based on constant isoperm levels [25]. Five RH dependent levels representing acceptable environments for museum locations with increasingly relaxed control were determined. The EWO-G dosimeter response values, representing braking points between the acceptability levels, were calculated from the calibration equation with single parameter values for the levels as input. Table 5.1 shows the input parameter values for the levels, with expected higher degradation rates on higher levels. Due to the additive nature of the calibration equation and the generally similar oxidative effects of NO_2 and O_3, the values for NO_2 and O_3 in Table 5 were set to half those found from the literature.

Table 5: Environmental parameter values used as input in the calibration equation to determine EWO-G dosimeter response for acceptability – location levels

Calibration point – Acceptability location levels	Trigger values					
	NO_2 (ppb)	O_3 (ppb)	UV (m W/m^2)	T (ºC)		
				RH = 45 %	RH = 55 %	RH = 65 %
1 – Archive store	1	1.15	1	20.8	19.3	18.2
2 – Purpose built museum	2.5	3	3.75	22.9	21.4	20.2
3 – House museum	5	6.5	15	24.5	23	21.8
4 – Open structure	10	12.5	37.5	26.8	25.3	24.1
5 – External store with no control	15	25	37.5	29.0	27.6	26.2

6 EWO dosimeters as a part of preventive conservation strategy

Exposure of EWO dosimeters on location should be made together with a preventive conservation evaluation. When reading the result, the user should consult the interpretation diagrams that accompany the dosimeter. If the results raise concern about acceptability of the environment, a novel, systematic approach to diagnosing and mitigating problems has been developed in the MASTER project. The conservator should use the EWO dosimeter information together with all other available information, such as environmental monitoring, collection condition assessment, assessments of location suitability and risk assessment [26].

7 Conclusion

Results from the MASTER project will assist conservators working with the sustainable protection of the organic cultural heritage in museums, historical buildings and archives for the future, and help optimise the value of all the derived benefits in terms of economic, social and cultural utility. Continual consultation with European expert end-users ensured its relevance to European heritage conservation. The MASTER project contributes to competitiveness of European research and conservation technology, it contributes to the development of European environmental standards for organic objects on display or in storage, it increases the effectiveness in and benefits from investments in preventive conservation work, it supports the future return from sustainable heritage tourism and it indirectly supports the building of the European identity across time and national borders. Output from the MASTER project supports European Union policies in the field of protection of cultural heritage as expressed e.g. in Faro Convention (Framework Convention of the Council of Europe on the value of cultural heritage for society. 14. Oct 2005).

Until now, there has been no early warning dosimeters for organic materials, such as the EWO dosimeters on the market. The MASTER project has developed two new dosimeters for preventive conservation, involving innovation in science and application of existing technology. A major advantage of the new dosimeters is that the dose effect can be read directly at the location after exposure, and can be interpreted by comparison with threshold levels for acceptable exposure for different locations, from showcases to open displays. The MASTER project has developed a new preventive conservation strategy for organic objects based on the use of the new EWO system. The responsible conservation and administrative staff thus have full control of the process of evaluation of their environments, including dosimeter exposure, results reading and results interpretation based on preventive conservation and location knowledge. Further preventive conservation guidelines, as described in the Final Report from the MASTER project [1], will be made available for end users. By introducing this new preventive conservation strategy, the sustainable exploitation of cultural property can be enhanced.

The MASTER project has been a pioneering project in the field of systematic study of the combined impact of pollutants and environmental hazards on organic objects in museums, galleries, historic buildings and archives. It makes monitoring more systematic, more integrated with other preventive conservation methods, easier to understand and communicate as well as encourage analysis of data. Results from the project have filled current gaps in knowledge and contributed to preventive conservation in terms of new early warning technology for the monitoring of environmental conditions in museums, historic buildings and archives in the form of EWO dosimeters for organic objects. The MASTER project has developed and provided new technology, strategy and remediation guidelines to meet stakeholder needs. This will make it possible for conservators and managers responsible for the cultural heritage of European organic objects to make better-informed decisions about the most suitable preventive conservation methods, and to acquire knowledge about how changes in the environment will influence the performance of the protective measures. It will help meet economic and social demands by contributing to better and more cost efficient management and preservation of collections.

8 European project details

MASTER, EVK-CT-2002-00093, Preventive Conservation Strategies for Protection of Organic Objects in Museums Historic Buildings and Archives. Co-ordinated by Elin Dahlin, Norwegian Institute for Air Research, NILU.

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Dependency modelling for cultural heritage

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Key words: dependency model, mitigation, risk, preventive conservation

1 Introduction

Preventive conservation strategies have been developed to identify and monitor hazards to collections, through assessment of risk [1], environmental conditions [2] and condition of objects [3]. However, because the way in which we mitigate problems is often so varied, there is less published work on generalised techniques for mitigation. Valuable case studies on control methods and solutions to specific problems exist, but choosing the right approach can be difficult. Cost / Benefit Analysis [4, 5] is the only technique that addresses how to choose appropriate mitigation methods but it needs to draw upon existing, defined solutions in advance. However, risks to collections are dependent on the outcome of a chain of events which *can* be generalised. Like any process or chain, there are strong and weak links that will determine success or failure. It is the identification of critical points and pathways that leads to effective risk management.

The links in the chain are understood and monitored in a number of different ways (figure 1). These can be related to existing assessment methods that record different parts of the same 'chain'. What we assess is the impact, or potential impact, of this chain of events on an object or collection. Modelling the process in such a way allows the conservator to think strategically about the most effective way of breaking the chain, which is essentially the goal of preventive conservation.

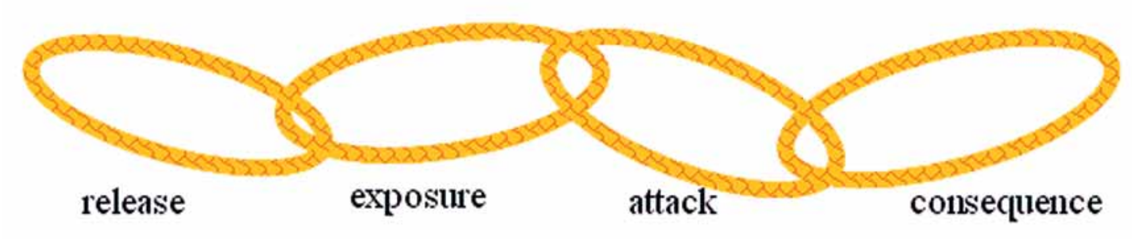


Figure 1: The risk chain: Various stages must be fulfilled before 'damage' occurs. Based on Covello and Merkhoffer [6]

Dependency modelling is a technique that develops this concept as a deductive 'top down' approach to analysing risks in systems. It involves specifying a 'top event', which is the outcome of a chain of events. This is followed by identifying everything that leads up to that event and all the ways in which that event can happen. Top events can be any identifiable outcome, positive or negative, as long as boundary conditions can be developed to model the process.

The technique was developed for cultural heritage as part of the MASTER project (Preventive Conservation Strategies for Protection of Organic Objects in Museums Historic Buildings and

Archives) [7], as part of the preventive conservation strategy. Its integration with diagnostic monitoring and other data in preventive conservation will be discussed later.

2 The process of dependency modelling

The technique was originally devised by Bell Telephones in 1962 in connection with the minuteman missile launch system and developed by Boeing. It has since been used for applications as diverse as nuclear reactor safety [8] to reliability of broadcasting methods [9]. Assessing the vulnerability of a system can lead to a broad understanding of, not only the events preceding an outcome but their relationship. An advantage of dependency modelling for catastrophic risks is that it does not imply that catastrophes are single events that are not influenced by the context in which they occur. This has been a problem in analysing conservation issues before. Jigyasu points out that earthquake disasters are not simply one event but should be viewed with the context that surrounds them [10].

A very similar method, fault tree analysis which models failure of systems, is the logical inverse of dependency and also relevant to discussion. But for heritage conservation, dependency model is a more appropriate term since there is less value judgement about the outcome. It has been used elsewhere to find areas in a process that require strengthening or contingency. It is adapted here to identify ways to reduce risks to heritage collections.

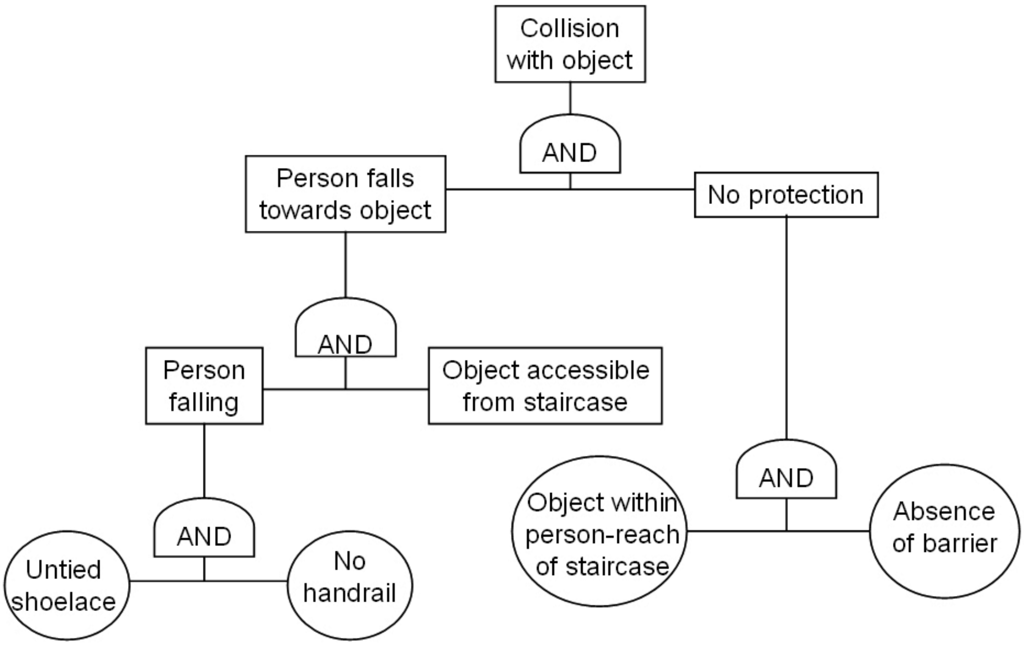


Figure 2: An example of a sudden event with preceding events

Dependency models can be applied to any process of which the user has a working knowledge, and fleshed out with specific information. It has a logical structure that can go into as much detail as required. The simple example above (figure 2) illustrates the points at which events take place and the relationships that lead to them.

In developing a dependency model of risks to collections, defining the top event is essential. Damage may occur in many different ways, with large or small impacts. In terms of deterioration, this may mean an acceptable level or rate of change. In these cases, the top event can be quantified. The conservator must declare the point at which the chain is ‘broken’. This can be based on technical information, such as a damaging level for a material present in the collection, or likelihood of catastrophe. It can be a more abstract concept, as long as there is an understanding of when the top event has occurred.

Definition of potential damage might require reference to a time period, so an acceptable rate or probability can be expressed. For example, Ashley-Smith et al. [11] defined levels of acceptability for lux levels in a year based on rate of change of different dyes and pigments. Concentrations or levels might be required to define problems with pollution or critical points of relative humidity for different materials.

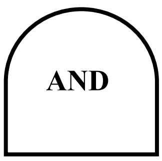
Framing a top event involves specifying the nature of the risk or system to a certain extent. By developing the processes involved for each risk, the specific factors relevant to an institution can be applied to the model. This can involve different kinds of information, sensitive to the context. The 'boundary conditions' of the model have to be defined in advance. The boundary conditions in the model are determined by the outcome. There may be many ways in which an event might occur, such as a statue breaking from earthquakes, vandalism or display conditions. The extent to which different events are modelled will depend on how far one wishes to examine. Equally, the level of resolution in the model can vary. Considerable detail of event causes may be required, and the preceding causes to be identified but this must be balanced with keeping the analysis on a manageable scale. This level of resolution will vary, depending on the reasons for the model and the situation.

2.1 Kinds of relationship

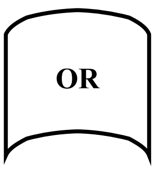
Dependency models are based on the notion that some links in the chain are easier to break than others. The strength of different links can be based on a number of factors and illustrates the novel approach of the model. The strength of a relationship depends on the number and influence of contributing factors. For an event to occur, the factors that contribute to it must take place at the same time. However, the contributing factors may come from a number of different sources. These issues build up the character of the model.

2.1.1 AND/OR dependencies

For the 'top event' to be successful, all of the lower events must be fulfilled. Figure one only shows one kind of relationship between events. However, there are two important types of relationship in a in a dependency model. These are defined as AND and OR relationships. If all factors are required for an outcome to occur, relationships are weak. Where alternative factors exist, relationships are strong. AND relationships are weak, since they are dependent on all of the contributing factors. OR relationships are strong because elimination of one contributing factor does not eliminate the relationship. Points at which elimination of an event might not mitigate the outcome can be identified by the presence of OR relationships. There may be any number of events leading to an OR relationship.



The output event occurs if all of the input events occur.



The output event occurs if at least one of the input events occur.

The point where these prior events meet, where the AND or OR symbol stands, is referred to as the *logic gate*. Causality never passes through an OR gate [12] – the input faults are never the causes of the output faults – they are identical to the output but more specific. For example, open windows, open doors and uncontrolled heating are all specific versions of uncontrolled relative humidity. AND gates *do* specify a causal relationship [12], for example unstable storage box and a high shelf lead to the output of an object falling to the floor.

There are variations on these gates which have been created to add sensitivity to the modelling. Some of them are useful to conservation. All of them are variations of the AND or OR gates.

- Priority AND – All take place in a sequence
- Inhibit – Conditional factors (AND + the condition). Deposition of pollution on some objects may be affected by RH levels, or pest infestations only take place in certain RH conditions. This is usually expressed as a hexagon.

2.2 Kinds of event

There are various different kinds of event, which are characterised to illustrate their role in the model. It is useful to distinguish between an initiating event, which requires no previous causal information and intermediate events, which are the consequence of earlier events occurring.

- Top event – the event that signifies that the process has reached a conclusion in terms of the system boundaries. The definition of a top event may require some indication of time or values to indicate what constitutes occurrence and what doesn’t. The top event can be anything, tangible or intangible. It may be an object breaking from physical damage, or simply the impact of physical force on an object. It can be tangible or intangible, positive or negative as long as preceding events can be identified. These as usually represented as rectangles.
- Intermediate event – an event that occurs because of one or more antecedent causes acting through logic gates. These are most of the events that lead up to a top event. These are usually also represented as a rectangle.
- Initiating or basic event – a basic event requiring no more development under the model. An initiating event may be the source of a hazard, such as artificial light, or a point at which the institution has control over a hazard, such as daylight entering a museum. They require no further development for the model. These are usually represented as circles.

2.2.1 Other kinds of event

Other types of event have been developed to help illustrate the process in the model, which can include information on how activities occur. These are less common features of dependency models.

- Conditioning event – this is a modifying factor, which is usually used in connection with ‘Inhibit’ relationships mentioned above. It is used to record restrictions or limits that might apply to any relationships within the system. Environmental effects on reactions are examples of this kind of event. These are usually represented as ovals.
- Undeveloped event – an undeveloped event is an event that is not examined further because information is unavailable, or because the consequences are insignificant. As a result, the sources and definitions are not well defined. Improper installation of equipment is an example of this. These events are usually represented as diamonds.
- External event – this is an event that is usually constant, expected to occur and outside the control of the modeller. This is an event which is not necessarily a positive or negative factor but will influence the outcome of the events, such as relative humidity

reaching dew point which could lead to interstitial condensation or condensing dehumidification. They are usually represented as a house shape.

External information about the process can be useful for a number of reasons. External events, such as the psychrometric changes in air are useful to understand and illustrate the process, and can also help assess the effects of possible mitigation methods, such as refrigerant dehumidification. An example is given in figure 3, below. By including technical information, and knowledge about the context, the model is supplemented with information that makes the model more sophisticated.

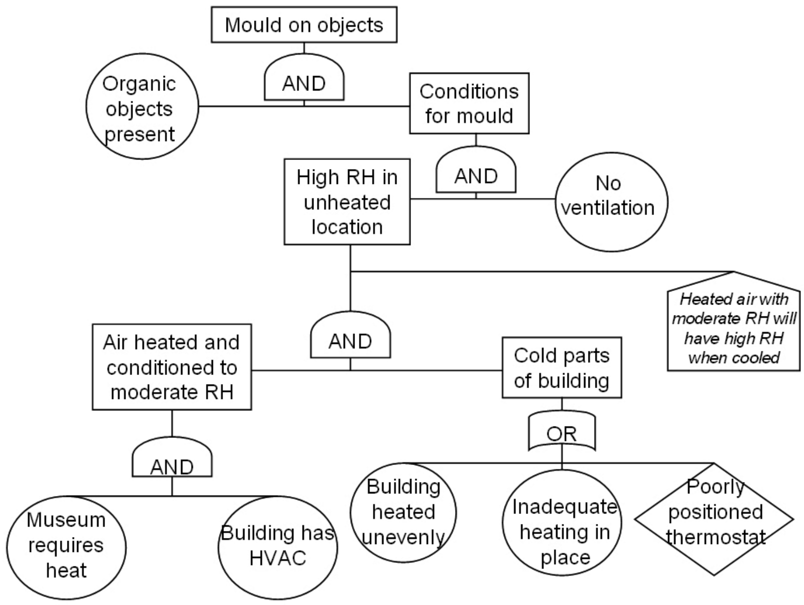


Figure 3: A dependency model with an external event helping illustrate the process being modelled

3 Deterministic risks

The nature of the dependency model appears to be more suited to catastrophic risks, where events either happen or don't, rather than gradual or cumulative risks. There is no directly definable event for deterministic risks but the build up of damage over time. There is also the fact that the rate of these 'events' can be influenced indirectly. For example, the deposition rate of pollution can be influenced by temperature and RH. Their presence alone will not result in the success or failure of an event but a decrease in temperature and RH will reduce the reaction rate. As a result, both the event itself, and relevant relationships do not have Yes-No functions to suggest that the chain is intact or broken.

However, the levels of preservation to determine acceptable and unacceptable environments can be used to define the point at which the event is successful (i.e. damage takes place). By providing a quantitative description of acceptability, the top event can be given a point at which it is considered to have been reached. Determining a level of acceptability means one has the ability to define the event. This means that the deterministic qualities can be modelled. This kind of categorisation is common in risk management and preventive conservation. Existing standards can be used to develop such steps, particularly where thresholds have been established. These should be related specifically to the materials and the risk being modelled.

3.1 A simple example based on a European museum

Taking a dependency model for NO_2 (figure 4), based on a European museum with a heating, ventilation and air conditioning (HVAC) system, one can see various points at which the risk can be mitigated. The weakest points in the model appear to be quite specific. As the tree gets lower down, from exposed surfaces of objects to ingress from external sources, the relationships are more general. As a result, there are more alternatives that are available to completion of those events. These general issues can be further broken down, such as defining different possibilities for natural ventilation. The level of detail can be defined by the institution. Currently, all of the lower level relationships are OR relationships, which are harder to break. Monitoring of a location can allow some of these events to be eliminated, so OR relationships become weaker AND relationships. As a result, there are clear points where mitigation can have a significant impact on the rate of level of NO_2, reducing it to an acceptable level.

A level of 5ppb is given in the example, which is suggested as a level of acceptability for purpose built museum galleries in the MASTER project. The value was based on existing research into the effects of NO_2. Typical organic plant dyes on silk and cotton change within one year at this level, and natural organic colorants on paper change after five years [13, 14, 15].

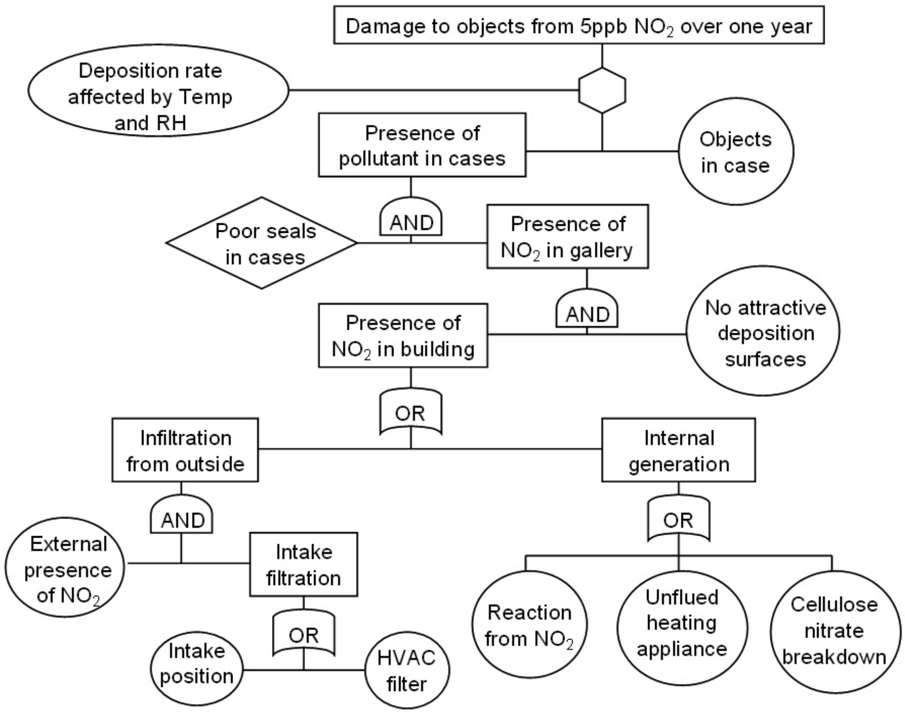


Figure 4: A model for exposure to nitrogen dioxide for a museum with an HVAC system, including an inhibiting relationship for the deposition on objects. Note the conditional AND relationship (hexagon) at the top of the diagram

One can see various ways in which the chain can be broken, including reduction of the deposition rate by lowering temperature and RH, expressed as a condition in reaching damaging levels for objects. Factors such as deposition of pollutants on surfaces before they are exposed to objects can be taken into account also. The less likely internal generation of pollutants is also included in the model.

It can also be seen that the nearer to the top event one looks, the more localised the mitigation. Relationships, or links, near the top event might require manipulation of showcases with pollution scavengers or different seals but this will have to be carried out for all cases. Events lower down include broader issues, such as pollution infiltration which may be harder to manipulate.

4 Including data in the model

Preventive conservation information can be directly placed into the dependency model. Data from techniques such as diagnostic monitoring can reduce some of the options provided, and determine other critical points in the system. This can help determine probabilities and provide information about which events can be eliminated to simplify the model. If the 'top event' is quantitatively defined, monitoring can also determine when the risk has reached a level or rate that is acceptable to the institution.

Different kinds of context-sensitive information can refine a dependency model and help the institution to concentrate on the events that are affording deterioration. Events that are unlikely or irrelevant can be eliminated, and the weak points in the risk chain more easily identified. For example, the figure below is a general model of damage from NO_2 which has been reduced to make the model more specific to the context.

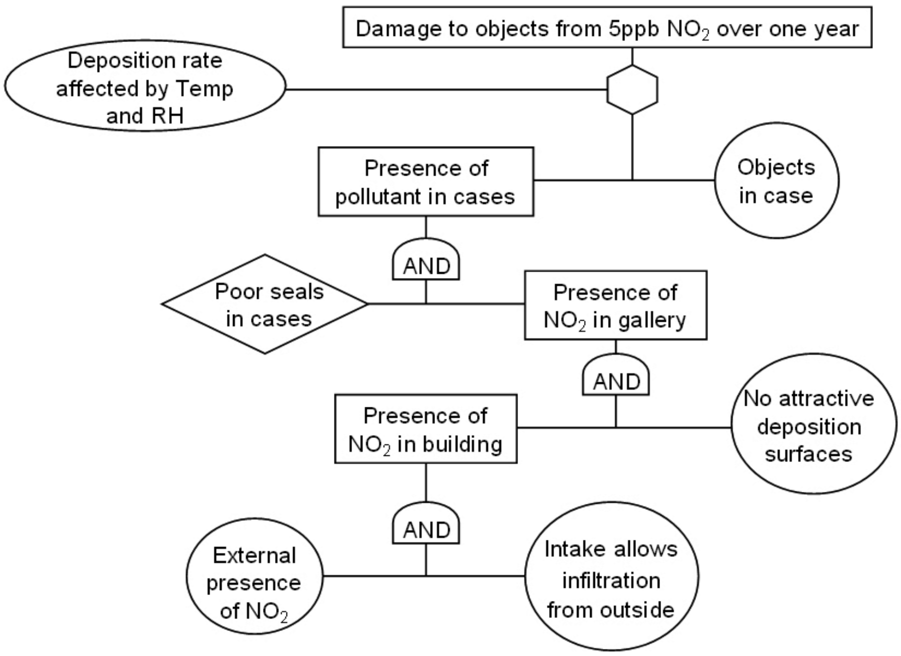


Figure 5: A reduced version of figure 4. The omission of some events is based on information from monitoring

The figure above is based on figure 4 but certain elements have been removed to make it more specific to a context. Information about the context can inform which of those relationships exist. For example, if the way in which pollution was entering a museum had been determined through diagnostic monitoring an OR relationship can be removed from the system, and the weaker AND relationship can be concentrated upon. As a result, the mitigation is better informed and the weakest link can be identified.

Risk assessment data can be applied to the model quite easily. Since assessment of risk is really looking at the same process in terms of threat, rather than mitigation, the information about different scenarios can be applied to determine the most appropriate course of action.

5 Probability

Once the tree has been constructed, probabilities can be applied to each of the events. Including probabilities increases the effectiveness and representativeness of the model. Since the outcome of all risks, catastrophic and deterministic, will depend on chance or situation, this can provide insight into different routes that might lead to the top event, referred to as cut sets. Determining the most cost effective way to break the risk chain, or decide which lower events should be attended to may depend on the probability of that event occurring. This can be achieved with scientific information, collected data and information related to the context. The different routes by which an outcome can be reached can be charted this way and the most probable identified. Events may be infrequent or only take place at certain times, and therefore difficult to model, but the construction of the tree can be altered for different contexts.

Cognitively, probabilities are difficult to reflect upon [16], since probabilities are treated differently with different relationships. Because AND relationships require both prior events the calculation is multiplicative. Because any of the preceding events in an OR relationship can ensure the outcome, the calculation is additive. The example below shows that probabilities for events are significantly affected by the kind of relationship.

AND relationships	$0.7 \times 0.2 = 0.14$
OR relationships	$0.7 + 0.2 = 0.9$

When connected, the whole model can have the effect of a Bayesian network from which one can infer causality, conditional probabilities, the most likely causes of an event, and modes and requisites for failure and success [17]. However, this is outside the scope of the paper.

6 Conclusion

Preventive conservation strategy has often provided useful, generalisable ways of determining the problems that conservators face. However, their mitigation has not received as much attention in terms of techniques that can be applied to different situations. The technique of dependency modelling offers a novel way of looking at how threats to collection preservation can be dealt with systematically and offers and approach to deciding on how identified problems might be mitigated.

Dependency modelling creates a deductive method for determining events, and a visual representation of the system. This can help understand and explain the appropriateness of different courses of action against risks to collections. Through the application of probabilities, a basis for quantitative analysis is provided. The technique identifies critical aspects of system behaviour and can be applied to any kind of system.

Development of a model tree does require a certain amount of expertise about the system but adaptable templates could feasibly be created for common situations. The process can also be time consuming but software has been developed to chart dependencies and calculate probabilities.

The model can be directly applied to European cultural heritage, and is intended to accommodate a wide range of applications. The illustrative examples are based on heritage institutions in Europe, but applications can be wider ranging. As well as modelling deterioration, one can use the same process to assess the reliability or effectiveness of mitigation. By making the aim of the mitigation the ‘top event’, the processes involved in the chosen method can be modelled as the prior events. ‘Success’ in the preservation of cultural heritage may be abstract to a certain extent, but dependency models have accommodated many abstract applications.

Because of its potential to be applied to any kind of heritage, and any kind of situation, dependency modelling has a great deal to offer conservation. The development of a method to select appropriate mitigation methods can lead to improved decision-making that is more transparent, and hence justifiable, and more cost-effective.

7 European project details

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Impacts of crushed rock quarries on historic villages and cultural landscapes

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Key words: aggregates, historic environment, noise, dust, vibration

1 Introduction

Annual production of crushed rock aggregates across Europe is currently 3000 million tonnes, a figure which is expected to increase over the next few decades with increasing demand for building material. For geological reasons many sources of aggregates occur in upland areas often within areas of great natural beauty with vulnerable cultural landscapes, archaeological sites and historic buildings. This paper describes research to investigate the physical impacts of extraction and transportation of aggregates on the fragile historic landscapes of England. The impacts of noise, vibration and dust on buildings and the quality of the environment are investigated at two case study sites, representing areas where large aggregate quarries are operating in close proximity to historic villages and landscapes.

In England many of the aggregates quarries are located in or close by to areas designated as National Parks due to their quality of natural and cultural landscape. For instance in the East Midlands out of a total of 2166 Crushed Rock Permissions, 284 fell within the Peak District National Park, whilst in the Yorkshire and Humber region, 149 Crushed Rock Permissions out of a total of 471 were in a National Park. The vast majority of these were in the Yorkshire Dales National Park with a few permissions in the North Yorkshire Moors National Park. The trend towards the exploitation of larger quarries in remote areas and the closure of smaller local quarries as these have become uneconomic resulted in aggregates being transported over much greater distances than previously. In 1997 road transport accounted for 94.5% of these journeys, with the remainder consisting of rail (5%) and water (0.5%). So as well as the direct impact of quarrying, road transportation is also an issue of concern.

2 Potential quarry impacts on the historic environment

The main environmental impacts of hard rock aggregates extraction and transportation on the historic villages and cultural landscapes were identified as noise, vibration and dust.

2.1 Noise impact

Noise, whilst not actually harmful to the physical historic environment, reduces the quality of life of communities and the quality of the experience and enjoyment of visitors to historic areas. Noise generated at open sites such as crushed rock aggregate quarries can, depending on distance, surrounding topography and prevailing wind direction, be transmitted beyond site boundaries. Sources of noise at crushed rock quarries include:

- Mobile plant (e.g. Excavators, front loading shovels, dozers and haulage vehicles)
- Static plant (e.g. permanent processing plant)

– Semi-mobile plant (e.g. mobile processing [figure 1] and screening plant)
– Road wagons transporting material to market / depots (figure 2)


Figures 1 and 2: Mobile processing plant at Arcow Quarry, North Yorkshire (left) and a quarry wagon crosses a historic bridge, Horton in Ribblesdale, (right)

2.2 Dust impact

Rock dust can be emitted from passing aggregate lorries and then distributed further a field by re-suspension by other vehicles, pedestrians and the action of the wind. Most rock dust will consist of fairly large particles, which cannot travel very far before falling out of the atmosphere due to gravity. However smaller particles will also be generated and these could be transported much further because they are not so readily deposited from the atmosphere. Two main damage effects to the historic environment are likely to be caused by rock dust:

– *Soiling* is the visible dirtying of building exteriors, interiors, furnishings and fittings due to the accumulation of dust. Many quarry dusts will be light in colour and therefore show up more clearly on dark materials. Soiling may be harmless in itself, but it could necessitate frequent cleaning in order to meet aesthetic expectations.
– Dust can also bring about *chemical attack* on some materials. An accumulation of surface dust may increase or deplete the moisture content of the surface; rock dusts (e.g. from limestone and sandstone) are likely to be alkaline in nature and possibly chemically reactive on a wide range of surfaces.

There is no universal size definition for dust, although for industrial emissions it's usually understood as comprising organic and inorganic particles with a diameter in the size range 1-75 μm [1]. Particles less than 1 μm in diameter tend to behave more like gases than solids and are referred to as 'fumes', due to their size these particles have a long airborne residence time. Particles which are above 75 μm are known as silt or sand and have a very short airborne residence time. As a result of quarrying activity, a range of dust particles are produced and can be transported outside the quarry location according to their mass and size. The distance dust particles can be transported also varies according to meteorological conditions and surrounding topography. It is important to note that dust is always present in the atmosphere and quarrying is just one source, other sources include combustion (e.g. fires, power stations and motor vehicles) and building and demolition work [2].

Dust particles can be produced at the following stages of mineral working:

– Soil movement – soil stripping and storage
– Overburden excavation
– Mineral type and moisture present

- Blasting events (figure 4)
- Mechanical handling of minerals such as during crushing and grading
- Vehicle movements on roads on and off site

2.3 Vibration impact

Vibration causes several types of damage to historic buildings and monuments: physical separation and cracking of renders and plasters; failures and cracks in the building fabric; gradual or slow movement of objects inside buildings, for instance those located in display cases or on shelves. Vibration can be transmitted from aggregate activity through air, within the range 20 Hz – 20 KHz, this manifests itself as noise. However, this research is interested in ground borne vibration which moves through the ground and can affect historic buildings and structures. It is supposed that over long time periods, load reversals can result in damage to delicate historic finishes such as renders and plasters. When amplified through the height of a structure or as a result of responsive floors, there is some evidence that ground borne vibrations can result in museum exhibits moving along surfaces.

Blasting of hard rock is the most common source of vibration in aggregates extraction, a source which is eliminated in sand and gravel extraction. Some ground borne vibration can also be generated through processing plant and vehicle movement. For example wagons climbing steep hills in villages (figure 3).

Figures 3 and 4: Quarry wagon ascending hill within the historic village of Cromford (left); dislodged material after a blast at Horton Quarry (right)

3 Case study methodology

The case study sites were chosen so that the impact on the historic environment of both aggregates extraction and transport, often along small country roads and through towns and villages, could be considered and for a methodology that can be replicated elsewhere, to be developed. The project identified three possible case study areas where there was deemed to be an established interaction between aggregate quarrying activity and the historic environment through noise, dust and vibration as described above. This was achieved through consultation with:

- The British Geological Survey (BGS), contractors on the project to undertake the dust analysis work. Access was gained to a database containing details of British aggregate quarries and through the Directory of Mines and Quarries (Cameron et al, 2002)
- Ordnance Survey (OS) maps and Geographical Information Systems (GIS)

- English Heritage, who funded the project through the Aggregates Levy Sustainability Fund (ALSF), predominantly the ALSF Advisers were consulted
- Local authority representatives (e.g. mineral planning officers and conservation and design officers), who were able to indicate areas of potential interest

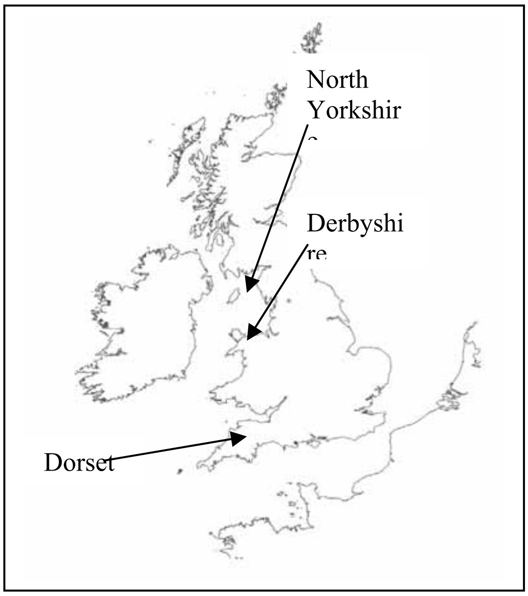


Figure 5: Geographical locations, within the UK, of the three areas where scoping visits were made to determine specific sites to investigate during the project

Scoping visits to the three possible areas, two in upland limestone areas in the North of England where crushed rock is quarried, the Yorkshire Dales and Derbyshire (figure 5). The other area was the Purbecks in Dorset, a low lying coastal area of southern England where sand and gravel is extracted. After visiting these areas it was acknowledged that two specific sites in the North of England stood out as displaying the interactions which would be most suitable to the projects objectives.

The quarrying activity in Dorset was interesting, there was also an important surrounding historic environment and the contrast between the two aggregates would have been interesting to investigate. However, the quarrying activity in this area was on a much smaller scale and didn't exhibit the direct interaction which was found at other sites.

The two case study sites selected were Horton in Ribblesdale in North Yorkshire and Cromford in Derbyshire, both produce crushed limestone aggregate. The Quarry in Horton in Ribblesdale, Horton Quarry, began operating in the 1880's, it is currently permitted to extract 600,000 tonnes per annum. The village (figure 6) has several listed buildings and bridges and is located, in some parts, a matter of metres from the perimeter of the quarry, although this isn't the boundary of extraction activities. The transport route for quarry wagons from the quarry runs through the village en route to depots and markets further south. Cromford holds significant cultural and historical importance. It lies within the area known as the Derwent Valley Mills, a World Heritage Site designated for its links with Richard Arkwright's pioneering cotton mills, dating back to 1771. Dene Quarry in Cromford began operating in 1947 and currently extracts 850,000 tonnes per annum. The village (figure 7) has a high concentration of listed buildings, many of which are in close proximity to the quarry perimeter and lie within the transportation route for quarry traffic.

With the help of the project GIS and local knowledge, properties of interest identified during the scoping visits were contacted by post to ask for access to their properties during the project. A good response rate ensued, resulting in properties closely fitting the project criteria in terms of proximity to quarrying activity and transportation and historical value were selected.

3.1 Monitoring techniques at case study sites

3.1.1 Dust

The measurement strategy was a combination of short-term active sampling of airborne dust to understand how particle concentrations varied over a few hours and hence the influence of factors such as working hours and traffic levels on local dust concentrations; and passive sampling of deposited dust to assess seasonal effects and compare deposition rates at different heights and inside and outside buildings. By subjecting these dust samples to analyses which would establish mineralogy and morphology it was hoped the origin of the dust could be established

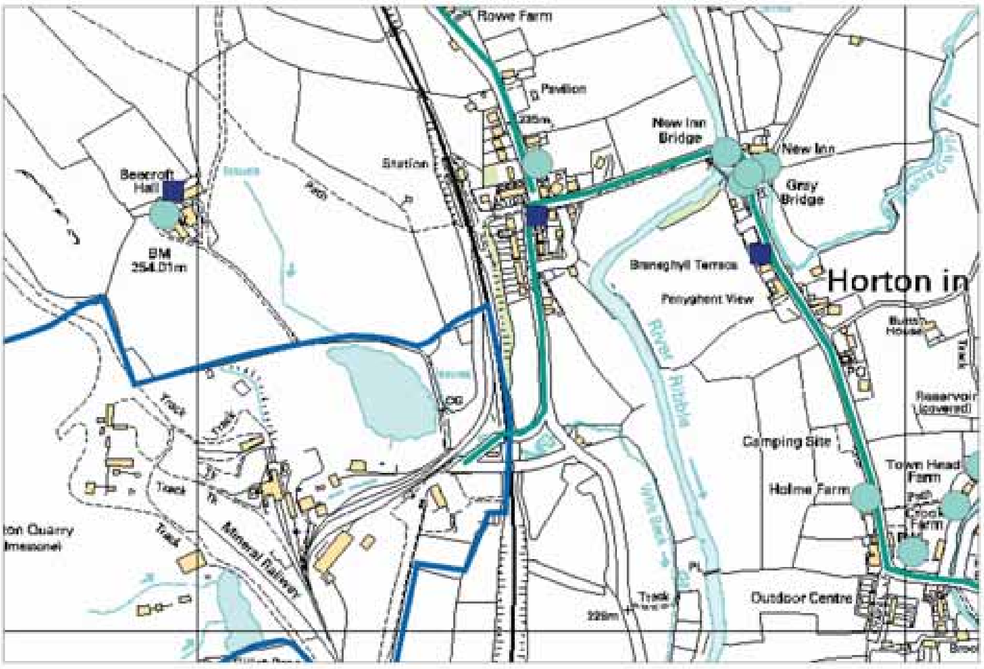


Figure 6 and 7: GIS output maps of case study sites, Horton in Ribblesdale, North Yorkshire (top) and Cromford, Derbyshire (bottom). Circles = Historic listed buildings, Squares = project monitoring sites. The solid lines drawn along roads indicate quarry transport routes. On each map the quarry boundaries, bottom left corner are marked with a solid line.

For the collection of deposited dust small adhesive tabs, mounted on 11 mm scanning electron microscope aluminium stubs were attached to the interior and exterior of the case study buildings. This method has previously been employed by British Geological Survey (BGS) and is similar to the method used by Yoon and Brimblecombe [3] to collect deposited dust inside museums and historic houses. The adhesive surface of each stub was exposed to allow uninterrupted dust settlement to occur during the exposure period. The stubs were positioned on selected walls in a vertical profile at 0.2, 1 and 2 m heights above ground level. Stubs were assembled in this formation for the winter and summer sampling campaigns and retrieved after 6 weeks and then delivered to BGS for analysis.

Suspended atmospheric dust particles were counted inside and outside at each selected property using an optical particle counter (Grimm Portable Dust Monitor Series 1.100). This instrument uses a pump to draw in air and a laser technique to count the particles the air contains, the particles are classified into eight size ranges, from 0.75-15 µm and > 15 µm. A measurement for each size range is logged every minute, enabling a real time picture of the variation in dust concentrations over a time period to be built up. The particle counter was deployed for 2-3 hour periods at each of the case study sampling sites.

3.2 Sound intensity meter

Two different units were used to measure the sound intensity. The first, an inexpensive hand-held unit gave an instantaneous reading integrating the sound intensity over the last second in time. A second unit with the facility to log the aggregated sound intensity over a given period was used. The collection period was set at the lowest possible value of 1s to characterise most effectively the “soundscape” at each location. In both cases, the reading is given with respect to a decibel (dB) scale which is related to the logarithm of the ratio of the change in pressure which manifests itself as sound to the pressure representing sound at the threshold of perceptibility. A change in sound intensity of 10 dB represents a doubling / halving of the underlying pressure parameter. In all cases the sound measured is weighted so that, as far as human perception of the nuisance is concerned, the reading is independent of the frequency – or pitch – of the sound. The World Health Organisation recommends noise guideline for inside dwellings in day time and evening to be 35 LAeq, T dB and inside bedrooms during the night to be 30 LAeq, T dB. Outdoors, the WHO suggests 55 LAeq, T dB as being the level at which noise becomes annoying [4].

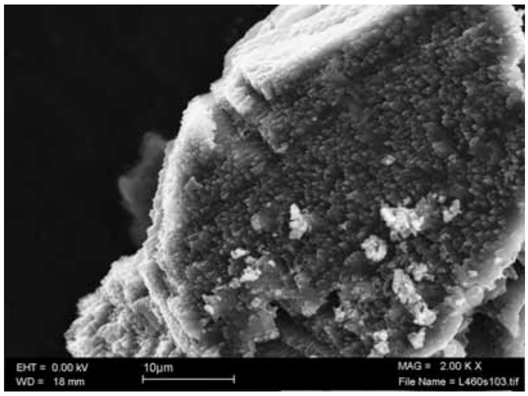
3.3 Vibration

A Vibrock seismograph was used to establish the ground borne vibrations as close as possible to the foundations of the buildings being examined. The transducer itself is a geophone which gives a readout of vibration in terms of velocity (mm/s). The unit was set to trigger at 0.1 mm/s. In other words, the unit would start collecting information about vibration experienced by the geophone as soon as the level reached 0.1 mm/s. This was the lowest trigger level available and was close to the resolution of the instrument.

4 Results

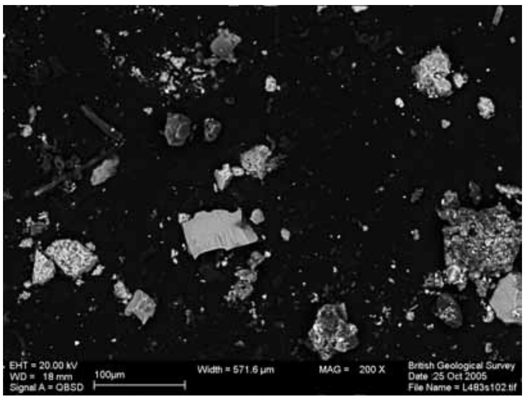
4.1 Dust

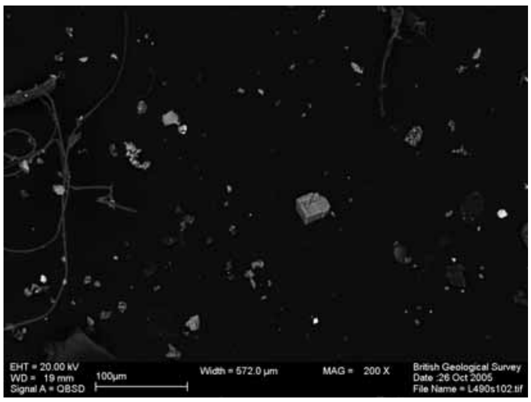
The passive dust samplers were analysed using a Leo 435VP scanning electron microscope. The general appearance of the samples and individual particle morphology were studied on digital images of the stubs, recorded at x50 and x200 magnification. An Oxford Instruments ISIS 300 energy-dispersive x-ray fluorescence spectrometer was used to qualitatively analyse the chemical composition of particles. Samplers from 1m height indoors and outdoors were analysed using automated image analysis, based on the KS400 Petrographic Image Analysis system, to count the number of mineral particles on a representative area of the samplers. Studies of the inorganic particle morphology and chemical composition found that calcite particles dominated the outdoor samples from both Horton and Cromford. Calcite is the main mineral constituent of the limestone rock that is quarried at both sites, though it can also occur in soils formed by the natural weathering of such rock. Close examination of the calcite particle morphology showed that many particles had an angular appearance with sharp edges, as if cut in some mechanical process (figure 8). This is consistent with them being freshly formed in aggregates crushing processes at the nearby quarries. It is interesting to note that village residents at Cromford commented that dust deposited on vehicles had to be removed carefully as it was sharp to the touch and could easily scratch paintwork. Other particles were well-rounded and showed evidence of etching from rainwater dissolution, indicating that they have probably been in the environment for a longer time, or may be derived from soils (figure 9).



Figures 8 and 9: Calcite particles from outside 2 Bransghyll Terrace, Horton (left): angular particle, possibly from quarry processing, (right): weathered particle

Indoors, the passive samplers collected a larger proportion of organic material, such as hair and fibres, and fewer mineral particles, as illustrated by figures 10 and 11 which compare representative areas of outdoor and indoor samplers. Table 1 shows the mineral particle indoor / outdoor ratios, calculated from the automated image analysis particle counting, for different size ranges of particle. In most cases fewer mineral particles were deposited indoors than outdoors at each of the sites, though the reverse is true at 101 Cromford Hill during the summer and for one measurement at 14 North Street. Indoor sources of mineral particles may explain this – there was evidence from the SEM analyses of indoor particles from plaster, metal, ceramic and laundry product dusts. However, calcite was still found in significant levels in almost all the indoor samples examined.





Figures 10 and 11: x200 magnification SEM photographs of samples from 14 North Street, Cromford (summer monitoring) left: outdoors, right: indoors

Table 1: Indoor / outdoor ratios of normalised particle counts (per mm^2 per 4 week collecting period) for the particles deposited on the sticky samplers 1 m above ground level

House	Particle size range (µm)	Summer	Winter
2 West View Terrace, Horton	1-10	0.14	0.23
	10-100	0.39	0.42
14 North Street, Cromford	1-10	1.10	0.66
	10-100	0.47	0.28
101 Cromford Hill, Cromford	1-10	1.45	0.53
	10-100	1.38	0.73

Figure 12 compares the airborne dust concentrations measured at the two case study sites on week days and at the weekend, when quarry activity is either absent entirely or very much reduced. The house at 2 West View Terrace is located on the direct access road to Horton Quarry (figure 6). The only through-traffic to pass this house is either entering or leaving the quarry. On the Thursday, an operating day, the dust concentrations are characterised by many short-term large peaks.

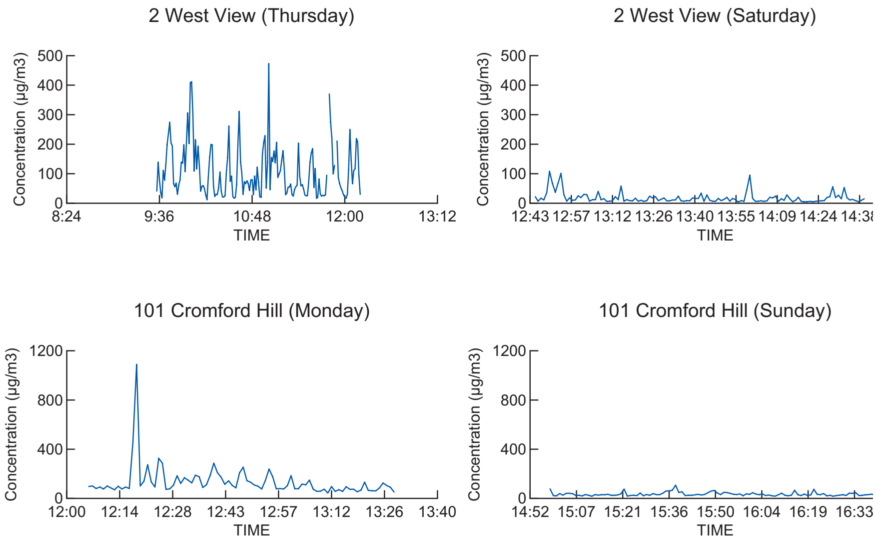
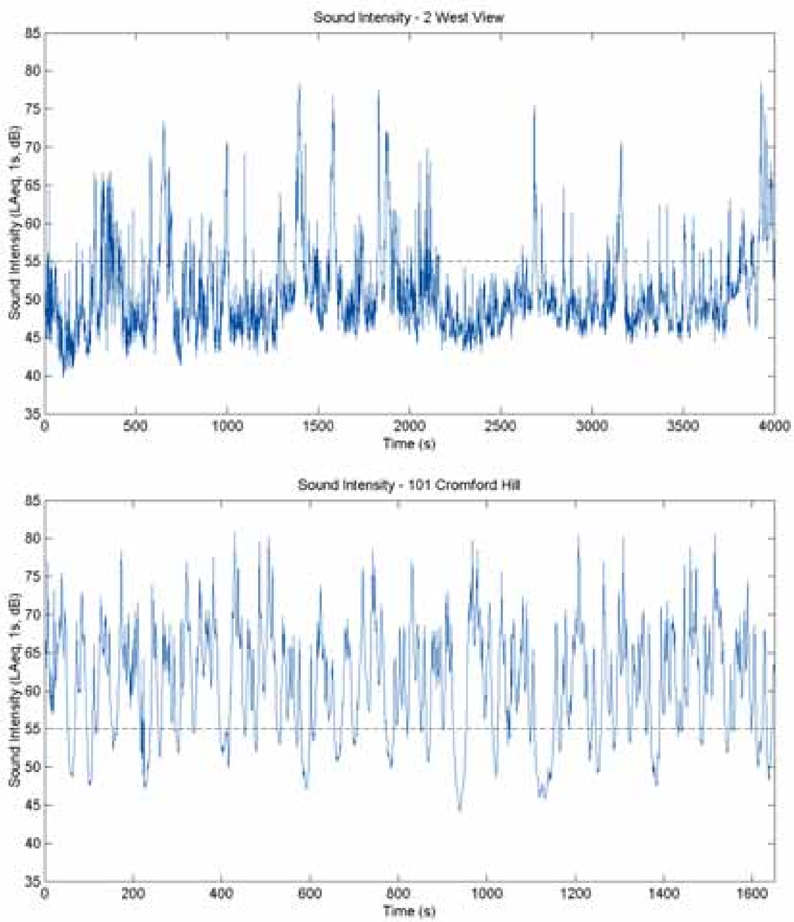


Figure 12: Real-time Grimm optical particle counter measurements of total airborne dust concentrations at 2 West View, Horton (summer) and Cromford (winter)

An examination of the size distribution of this data (not reproduced here for reasons of space) showed that the peak concentrations contained a greater proportion of large particles than the background dust, consistent with the peaks being caused by heavier particles resuspended to the air by passing vehicle wheels, or given off by the vehicles themselves, which then quickly redeposit on the ground and other surfaces. On the Saturday, when the quarry was not working, both the peak and background concentrations were much lower. This pattern is also evident, in the data from Cromford, where a much lower concentration is measured on a Sunday compared with the Monday. During all these measurements the weather conditions were similar: being dry with very little wind. These data suggest that airborne dust levels are increased by passing quarry traffic at 2 West View, Horton, but the situation is less clear at Cromford Hill, where the road is busy with many other vehicles apart from quarry wagons. These probably also contribute to the resuspension of dust deposited by quarry wagons or from other sources.

4.2 Noise and Vibration

Interpretation of the results from the sound loggers are ongoing. Figures 13 and 14 show raw data from two of the monitored locations. The readings in each case are immediately outside the building. It is clear that the property in Yorkshire experiences less noise when aggregated over periods of 1 minute or more. The values from Cromford appear to exceed the WHO recommendation of 55 LAeq, T dB. In each case individual traffic events unsurprisingly cause peaks in the graph. The readings are currently being compared with video footage which allows us to identify which of the peaks are associated with aggregates traffic. This would then permit an indication of what proportion of the sound-loading results from this source.



Figures 13 and 14: Shows raw data from 2 West View, Horton in Ribblesdale (top) and 101 Cromford Hill (bottom)

5 Conclusions

The mineral composition and morphology of dust detected in the outdoor atmosphere at Cromford and Horton indicates that a large component of it comes from quarrying. Our preliminary analysis suggests that quarry dust is distributed along transport routes by quarry and other vehicles, and deposited on or nearby to historic buildings. It is probable that the amount of dust deposited in this way is much less than in past decades because wagons leaving the quarries at the case study sites are required to be sheeted and also the vehicle wheels are washed as they leave the quarry site. These measures are required in the quarry operating conditions agreed with the local authorities and are strictly enforced by the quarry managers. The main mineral phase in the dust is calcite, a calcium carbonate ($CaCO_3$) mineral that is alkaline in nature. This dust could be potentially reactive or corrosive on sensitive collections indoors but is unlikely to have any chemical effect on nearby limestone buildings that are constructed of essentially the same mineral. Sharp-edged fresh quarry particles could be abrasive to soft or easily scratched surfaces, before they are weathered by the environment. There is evidence of quarry particles being found inside the houses studied, but further work is required to differentiate particles of quarry origin from other mineral particles found indoors. The data distributions of particles measured by active sampling will be further studied to see if this can contribute to our understanding of particle sources. The real-time data will also be correlated with traffic data and quarry wagon data despatch provided by the quarries themselves to understand the contributions of quarry and other vehicles to airborne dust concentrations in Horton and Cromford.

The seismograph unit was found to trigger quite frequently as a result of wagons related to the aggregates extraction industry passing by. Peak velocities (known as peak particle velocities or PPVs) of 0.375 mm/s were found. Results showed that unladen trucks were equally likely to cause measurable events. Little is known about the effect of the cumulative effect of prolonged exposure to low amplitude vibrations. However even the most conservative codes of practice regard the threshold of 0.5 mm/s as not posing a threat to structure – even those with delicate finishes. These findings are some-what counter-intuitive. There is a feeling amongst local residents that vibration from aggregates wagons is palpable and probably the cause of structural damage such as settlement. Our research does not find evidence for this view. The reason for the apparent large vibration dose is probably two fold:

- The ground-borne vibration is accompanied by air-borne excitation both audible and inaudible. The combined effect can be rather dramatic.
- Humans are rather sensitive to vibration – more so than the buildings they occupy.

Although not a European project, these results and the methodology employed will have Europe-wide relevance and applications. There are similar issues of aggregates extraction and transportation and their effects on cultural heritage across Europe.

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Impact of moisture sorption stabilization as a preventive conservation approach

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Key words: equilibrium moisture content, moisture sorption, air humidity control

1 Introduction

The reported research of microclimate adjustment in remote historical buildings arose on the occasion of rehousing the precious collection of 29 medieval paintings of Master Theodoricus in the Holy Cross Chapel at the Czech castle Karlštejn where they had previously been deposited for more than six centuries [1]. The paintings suffered serious damage due to moisture impact and had to undergo a costly restoration. Before their return to the Great Tower of Karlštejn a unique air handling device was developed and installed in the Chapel to prevent the paintings from absorbed moisture changes.

It is a characteristic feature of European cultural heritage that its preservation is intimately connected with reusing historical buildings. The castles, mansions, palaces, monasteries etc. serve as deposits of historical or artistic collections which are also, to some extent, open to the public. As for the Czech Republic historical interiors of more than 250 castles and mansions serve as deposit and exhibition rooms for authentic historical and/or artistic collections, as archives, historical libraries etc. In approximately one third of these buildings particularly valuable collections of paintings and sculptures are presented. Since neither a heating nor air-handling device is in operation in these interiors as a rule, these precious collections are exposed to significant harmful impact, particularly due to moisture and its consequences. As it has resulted from the investigations of the National Institute for Preservation of Cultural Heritage, approximately in one half of the castles in the Czech Republic where such collections are deposited the interior temperature sinks sometimes below the freezing point during the winter season. Only about 40 per cent of these interiors are fitted out with humidity measurements. Reusing historical sites to keep historical and artistic collections is common in many countries, and owing to this an invaluable part of European cultural heritage is exposed more or less to the damaging impact of an unsuitable microclimate in historical buildings, particularly to the *impact of air humidity*, [2, 3].

Basically the air humidity harmful impact is a matter of prime importance in preventive conservation intentions [3, 4] as regards the deposits in historical buildings. The humidity corrections in microclimate adjustment are applied e.g. in [5]. The air humidity results in an amount of moisture absorbed in porous and moisture sensitive materials which settles at an *equilibrium moisture content* (EMC). Just this absorption is the *primary harmful impact* on the state of the artefacts originating from the *changes* of *moisture content* absorbed in moisture sensitive materials, since these changes bring about an anisotropic *swelling* or *shrinking* which results in *deformations* or opening *cracks* in exhibits. Just to avoid the EMC changes in the most sensitive materials and in this way to prevent them from dimensional changes of the exhibits arising from the air humidity and temperature variations, it is essential to *keep the moisture* *content in the artefacts constant* and the aim is to stabilize the moisture content in spite of some temperature variations. In principle the usual daily temperature oscillations do not represent a serious threat to changing the moisture content because of very slow response of this phenomenon. However, temperature or humidity fluctuations with several-day duration may affect harmfully the moisture sorption conditions. To inhibit such impact an adequate air humidity adjustment preventing the moisture sensitive materials from moisture content changes may be the solution. Anyway, the smoother and slower are both the air temperature variations and the compensating humidity changes the more efficient is this kind of protection against the moisture change impact. The internal atmosphere permanently remains in almost steady conditions as to the moisture sorption and therefore no grounds arise to any change of the moisture content in absorbent materials at all. The aim of the paper is to present a novel technique of preventive conservation inhibiting the harmful impact of moisture content changes in unheated historical interiors by means of air humidity compensations.

2 Model-based equal-sorption humidity control

Although the primary significance of moisture sorption is evident the intent to introduce its control – in the usual sense – cannot be implemented simply due to the fact that the moisture content is not available as a measured variable. Furthermore, it is also to be pointed out that the moisture content cannot be considered as a parameter of the microclimate since it is an individual quantity appropriate to a particular material deposited in the considered microclimate. For each of the considered materials the moisture content u settles on a specific level, referred to as equilibrium moisture content u (EMC), appropriate to the relative humidity φ and temperature T of the ambient air. The EMC value increases with growing φ and decreases with growing T and, in general, it is considerably more sensitive to air humidity change than to varying temperature. Since only a long-term measurement can provide the EMC assessment the direct EMC control considerations are not feasible and only a model can provide a possibility to handle EMC as a matter of control. Various models, e.g. by Day and Nelson [6], Simpson [7], Henderson [8], are used to describe the relationship between the EMC as u, and the pair of air temperature T and relative air humidity φ, $u = \Psi(\varphi, T)$. Usually this relationship is displayed in the coordinates φ and u, as the so-called *sorption isotherms*, with temperature considered as a parameter. From various available models the logarithmic Henderson type of model, namely its three-parameter version

$$u = \left[\frac{-\ln(1-\varphi)}{A(T+B)} \right]^C \tag{1}$$

has been chosen as the most suitable from the viewpoint of the considered control. The symbols in (1) mean: $\varphi \in \langle 0, 1 \rangle$ is the relative air humidity expressed as dimensionless ratio, T is the air temperature in ^{o}C and u is the EMC expressed as the ratio of moisture mass content to the mass of anhydrous material. The parameters of the model are specific for each material, the additive temperature constant B is in ^{o}C, C is a positive dimensionless exponent less than one and the sensitivity coefficient A is in $^{o}C^{-1}$. Apparently the model is not suitable for air humidity getting near to the state of saturation, i.e. for $\varphi \rightarrow 1$ since then the logarithm is not defined. But any approaching the saturation state brings about condensation and thus such a state is quite inadmissible for the interiors concerned.

It is a problem for the proposed control idea that most of the models available from the references consider rather higher temperature levels than it is supposed in the preservation research. The temperature range of the microclimate adjustment in historical buildings is considered approximately from 5 ^{o}C to 25 ^{o}C, but for these temperatures the EMC characteristics are seldom available. It is necessary to mention that, particularly for wood, there are numerous references available dealing with equilibrium moisture content. However, taking use of them for the purpose of preventive conservation aims is advisable to be made with caution since a great deal of the published research has been tied up with the wood processing industry, particularly with the wood drying focused on the range of substantially higher temperatures than considered here. It is to expect that parameter *B* is rather lower in the lower temperature range than it results from higher temperature tests. Our EMC measurements in temperature range from 5 °C to 25 °C, see [10], proved substantially higher moisture sensitivity than can be found e.g. in [7]. We performed own experiments to assess the sorption isotherms for various sorts of wood and paper using the samples of various age – namely new and approximately hundred years old samples were used. These three week experiments definitely confirmed the expectation that not only the sort of the material but also its age and its state (how it is worn out) bring about significant changes in their sorption properties.

Model (1) has been designed for an assessment of moisture content in typical materials of historical and artistic exhibits. It is the main benefit of this model that it suggests the way of adjusting the microclimate conditions in order to provide the moisture content to be kept constant. It is apparent from (1) that for a temperature change from T_1 to T_2 a specific humidity change from the initial φ_1 to a new φ_2 could be provided that both these changes would cancel each other and the EMC value would remain unaffected, i.e. $u_1 = u_2$. Since just the change of moisture content is the crucial harmful impact originating from the air humidity this aspect is of primary importance in preventive conservation. Using (1) the requirement $u_1 = u_2$ leads to the following relationship dependent only on the parameter *B* (while *A* and *C* cancel themselves)

$$\frac{\ln(1-\varphi_1)}{(T_1+B)} = \frac{\ln(1-\varphi_2)}{(T_2+B)} \tag{2}$$

Hence, in other words, if the state of the interior air has changed from T_1, φ_1 to any other one T_2, φ_2 satisfying the equality (2) the material with the sorption parameter *B* used in (2) does not change its equilibrium moisture content during this change at all. The humidity adjustment $\varphi_1 \rightarrow \varphi_2$ cancelling the temperature change impact on EMC results from a simple rearrangement of (2) as follows

$$\varphi_2 = 1 - \exp\left[\ln(1-\varphi_1)\frac{T_2+B}{T_1+B}\right] \tag{3}$$

By the way, it also results from (2) or (3) that maintaining a constant humidity φ *cannot* be a microclimate solution for the moisture sorption stabilization if the room temperature changes substantially.

The intent to prevent the moisture sensitive materials from changing their EMC by means of compensating slow temperature changes by air humidity adjustments is founded on the knowledge that the EMC level is markedly more sensitive to the commonly encountered air humidity changes than to the usual temperature variations in historical interiors. As it can be shown on available sorption isotherms considerable temperature variations can be compensated by relatively minor corrections of air humidity given by equalities (2) or (3) and in this way the moisture content (in a selected material) can be prevented from changing its level. For example, in the pine wood, according to sorption isotherms in [4] a great temperature decrease, e.g. from 20 °C to 10 °C will cause no change in moisture content if the air humidity is made simultaneously to drop by about 4 or 5% and therefore this humidity readjustment is sufficient to avoid the swelling or shrinking of the exhibits made of this particular material.

The benefit of keeping the moisture content in the absorbent materials as constant as possible is evident from the preventive conservation point of view. Instead of the unavailable continual

EMC measurement an EMC model (2) can be utilized to prevent the EMC changes by means of humidity compensations. The control scheme – referred to as *equal sorption control* – stabilizes the moisture content in absorbent exhibits by means of a specific *humidity compensation just cancelling* the impact which would arise due to temperature variations. However, there is a crucial reason why the moisture sorption cannot be considered as a usual microclimate controlled variable. This reason is the fact that moisture sorption is not a microclimate parameter but a property of a *specific material*. For various materials, more or less, the sorption characteristics differ from each other.

The idea of preventing the moisture sorption from varying consists in the following. The control stabilizing the moisture content in the preserved exhibits is conceived as a reference tracking humidity control where the modestly variable desired air humidity value φ_D is assessed from the temperature and humidity measurements by means of the relationship (3), i.e.

$$\varphi_D = 1 - \exp\left[\ln(1-\varphi_0)\frac{T+B}{T_0+B}\right] \tag{4}$$

where T_0, φ_0 is a selected reference air state satisfying the preventive conservation standards and T is the actual (measured) interior temperature. This desired φ_D is applied as the reference setting for a humidity control adjusting the actual (measured) interior humidity φ towards φ_D by means an air handling device. Strictly speaking, as mentioned above, this control prevents only a single material – corresponding to parameter B considered in (3) – from varying the moisture content. But although various materials differ from each other in their sorption characteristics, it can be seen from (2) that the differences in parameter B values influence the needed humidity readjustment only weakly. Take, for instance, two materials M and N, having the sorption parameters B_M and B_N respectively, and suppose an air state change from the initial air state T_0, φ_0 to a different temperature T and try to assess the new desired humidity values as φ_M and φ_N for the materials M and N respectively. Using the equality (2) the following equations are obtained for both the materials

$$\frac{(T+B_M)}{(T_0+B_M)} = \frac{\ln(1-\varphi_M)}{\ln(1-\varphi_0)}, \quad \frac{(T+B_N)}{(T_0+B_N)} = \frac{\ln(1-\varphi_N)}{\ln(1-\varphi_0)} \tag{5}$$

The additive temperature constant B takes on relatively high values, say from 60 to 200 ^{o}C for various materials of the considered protected exhibits while, on the contrary, the temperature range supposed in this study is only from 5 to 25 ^{o}C approximately. Apparently, the higher B the less sensitive is the material to moisture sorption changes. It is easy to prove that the temperature ratios in (5) are close to one no matter that even substantial differences in B values exist. Consequently the humidity logarithm ratios are also close to one and therefore the required humidity readjustments $\varphi_M - \varphi_0$ and $\varphi_N - \varphi_0$ are of rather low values and cannot differ from each other substantially. For instance, the needed humidity readjustment for the pine wood differs only by about one per cent from the values appropriate for other sorts of wood, e.g. oak or beech etc. A similar conclusion can be arrived at for other moisture sensitive materials like various sorts of paper, canvas, parchment etc. With regard to attainable accuracy level of humidity measurements these *mutual differences are negligible* and the above assessed 4 or 5% readjustment of air humidity can be considered as satisfactory not only for wood at all but also for miscellaneous exhibits of paper, canvas, parchment etc. The only exception from this rule is a painting or an artefact on the interior wall. In this case the humidity readjustment needed to prevent the surface moisture content from varying are substantially higher than for the mentioned cases. Hence, as a general rule, the EMC variation is inhibited by humidity readjustments which are only weakly dependent on differences in the sorption properties of various materials.

The humidity adjustments resulting from the relations (2) or (3) may seem very modest. However their values cannot be viewed as such since they are to be compared with the *spontaneous changes of relative humidity* brought about by temperature variations. By differentiating the Magnus law [4] for the mixing ratio of moist air x,

$$x = 3.795 \cdot 10^{-3} \cdot \varphi \, \exp\left(\frac{aT}{b+T} \ln 10 \right) \tag{6}$$

with the parameters $a = 7.5$ and $b = 237.3$ °C, the condition of keeping x constant results in the following approximate relationship for a change from an air state T_0, φ_0 to another T, φ

$$\varphi - \varphi_0 \cong -\frac{a\,b \ln 10}{(b+T_0)^2} \varphi_0 (T - T_0) \tag{7}$$

For instance, if φ_0 = 0.5 and T_0 = 20 °C a temperature decrease, e.g. to T = 15 °C in a well insulated room brings about an *increase* of relative humidity by more than fifteen per cent. On the contrary, the humidity adjustment according to (2) or (3) requires to get at a *decrease* of φ by about 1.5 to 2.0% by the equal-sorption control. It means that instead of the natural tendency to *inverse proportionality* between φ and T increments in a well insulated room, a *direct proportionality* between temperature and relative humidity is to be artificially provided in the interior. From this point of view, the humidity readjustment (2) or (3) brings about a more substantial intervention into the air state than it looks at first.

To conclude this section the principle of the equal-sorption humidity control consists in maintaining the relative humidity at the level given in (4) according to the temperature and humidity measurements. In comparison with the extremely slow dynamics of moisture content changes it is easy to see that the proposed air handling process is relatively much faster, therefore the humidity correction can easily prevent from the moisture sorption changes in advance and the control is endowed with a *predictive character* in this way. The air-handling devices are designed as local apparatuses, portable at the best. In such a case the staff can optimize their location in the interior.

3 Implementation in Třeboň Archives

Already the first implementation of the proposed microclimate adjustment in The Holy Cross Chapel at the Karlštejn Castle has proved the ability to provide permanently favourable conditions for maintaining the absorbed moisture constant in most of the exhibits deposited in the medieval interior [1] in spite of extreme demands on visitors' intensity.

The second implementation of the proposed humidity adjustment is in operation in Historica Collection in State archives in Třeboň Castle, Czech Republic, using the original air-handling device. The equal-sorption control according to (3), is provided by an air-handling device, see Fig. 1. Let us mention that before installing the dehumidifying device into the collection room, its environment had been monitored for more than one-year period, see Fig. 2. As it results from the comparison of the measured relative humidity and its desired value computed using the Henderson model which would guarantee constant EMC only dehumidifying is needed. Thus, the air-handling device can operate and provide the favourable microclimate in this interior during the whole year.

For controlling the air-handling device a special control unit has been developed based on the microcontroller [9]. In the memory of the control unit a data table for predefined types of interiors is stored from which the program assigns the desired value of the relative humidity φ to each measured temperature sample T according to (3). Consequently, the desired φ_D is compared with the measured φ and on the basis of this comparison the program algorithm decides whether the air handling unit is to be switched on or off.

Figure 1: Interior of Historica collection in Třeboň archives with air-handling device

The first results measured in the controlled environment from July 17th to October 30th 2005 are shown in Fig. 3. As can be seen, for both materials paper and wood EMC are almost constant, which is in agreement with the primary aim of the control (as to the parameters of Henderson model (1) see [9]). Comparing the EMC characteristic in Fig. 3 with those in uncontrolled environment shown in Fig. 2 in the same period of time, we can clearly see the improvement brought about by the implementation of the control method described in this paper.

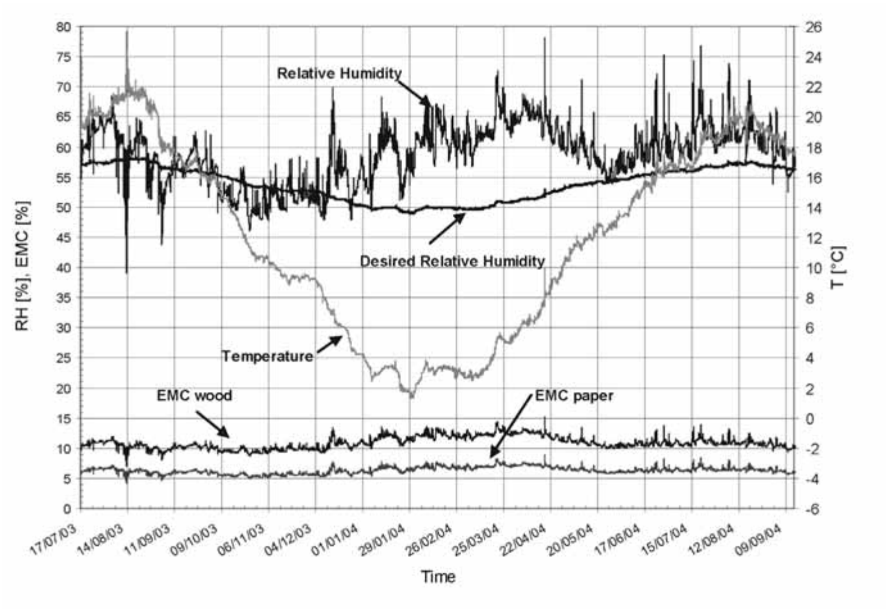

Figure 2: Records of the uncontrolled environment in Historica Collection of Třeboň Archives and the proposed relative humidity adjustment for desired EMC of pine wood $u_D = 10\%$

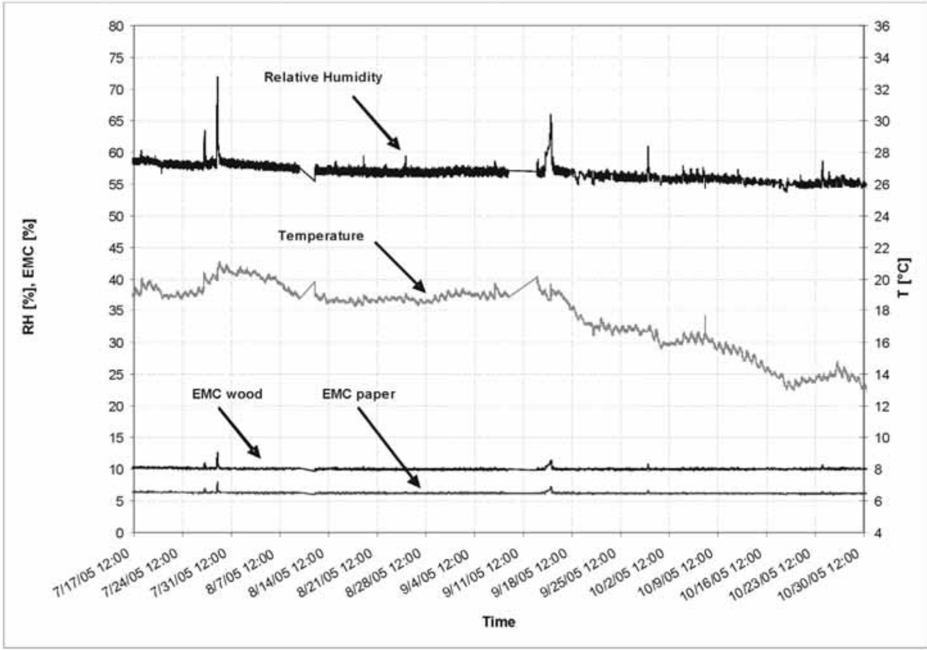

Figure 3: Records of the controlled environment in Historica Collection of Třeboň Archives

4 Conclusions

Due to the prevailing climatic conditions in most of European countries significant problems arise in preventive conservation of cultural heritage connected with the variability of moisture sorption particularly owing to the fact that a great deal of this heritage is deposited in historical buildings not equipped with either heating or any kind of air-handling device. The main objective of the proposed microclimate control is to prevent a broad class of preserved exhibits from moisture originated damage brought about by the variations of absorbed moisture. Although the interior temperature is left to run its almost unaffected natural yearly course its impact on moisture sorption is compensated by air humidity adjustments.

In principle the moisture content in the most significant materials is considered as the controlled variable, but since an acceptable method of moisture content measurement is not available a model-based control scheme is applied. From the requirement to keep EMC constant the air humidity to be adjusted by the control is assessed from both the air temperature and actual humidity measurements by the help of equilibrium model. Instead of the natural tendency to *inverse proportionality* between the temperature and relative humidity trends in an unaffected and insulated environment, the objective to keep EMC constant requires to make the interior relative humidity to be *specifically directly proportional* to the interior temperature. The desired humidity-temperature proportionality is based on the Henderson model of EMC with taking advantage of the fact that only *B* of its three parameters is relevant to the humidity adjustment.

The crucial point of the proposed microclimate adjustment consists in the finding that despite the differences in sorption characteristics for various organic materials such as wood, paper, canvas, parchment etc. the desired *humidity corrections can be considered as universal* for all of them. As the only exception from this rule the paintings or artefacts on the interior walls solicit a specific treatment. The correcting action of the equal-sorption control compensates the relative air humidity not only for the air temperature changes but also for the intake of moisture brought by the in-leakage flow of the outdoor air and by the moisture diffusion from the walls. It is peculiar for the most part of Central Europe that providing these humidity compensations needs almost all the time to rid the interior of a specifically varying amount of water per hour, only seldom a slight moisture supply is needed. Two implementations of the equal sorption control in a castle and archives have proved its ability.

5 Project details

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Developing innovative portable diagnostic techniques and approaches for the analysis of metal artefacts from museum collections

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Key words: metal artefacts, Mediterranean, LIBS, micro-XRF, X-ray radiography, non-destructive, technological and condition surveys

1 Introduction

PROMET is a three-year European 6th Framework funded project, priority INCO, which began in November 2004 with 21 partners from 11 countries of the Mediterranean basin. The main goal of the project is ensuring the survival of the outstanding metals collections throughout the Mediterranean region housed in museums. The environment in most of these museums are uncontrolled in terms of relative humidity, and contain aggressive agents that cause metal degradation, such as chloride salts. The vast number of metal artefacts in their collections and the high cost of repeated maintenance makes it impossible to simply place them in environmentally controlled areas or treat them regularly with protective coatings. The costs are simply prohibitive. The only way to establish and to promote a proper conservation strategy for the Mediterranean region is to develop prototype portable monitoring systems and safe and effective protection methods.

Advanced analytical methods can be used to survey large collections of metal objects in-*situ,* making it possible to pinpoint conservation needs without any risk of damaging the artefacts. Materials analysis techniques, such as laser-induced breakdown spectroscopy (LIBS) and micro X-ray Fluorescence (μ-XRF) are promising tools for identifying the characteristics of metal artefacts as well as the different metal degradation factors. LIBS is a rapid, nearly non-destructive elemental analysis technique, which is based on the characteristic atomic fluorescence emitted from a microplasma produced by focusing a high-power laser on a solid surface. It requires no sample preparation and the results can be acquired in a few seconds. Due to these advantages, it has been already used for the analysis of pigments in easel paintings, icons, polychromes, pottery, glass and metal objects verifying its capability in the field of art and archaeology [1, 2, 3]. The analytical capabilities of the X-ray Fluorescence (XRF) method (based on the detection of the characteristic X-rays emitted by an atom after its photoionization) have motivated rather very early, almost at the beginning of 70's, its implementation for the non-invasive characterization of museum collections [4]. The method has been also applied to all kind of ancient materials or artworks (metals, ceramics, glasses, paintings, inks, etc), providing simultaneously multi-elemental and sensitive compositional analyses. However, the large dimensions and cost of the early developed XRF spectrometers prohibited their extended use as a routine diagnostic tool for conservators working in a museum environment. At mid

90's, the breakthrough in X-ray instrumentation, particularly in the development of peltier cooled X-ray detectors, supported the development of portable and compact spectrometers with improved analytical performance and easy handling by non-experts [5]. Furthermore, the additional development of optical devices capable to concentrate X-ray beams down to few tens of micrometers has driven the microscopic analysis of surface details or the production of two-dimensional elemental distribution maps. The stationary μXRF analysis (with laboratory spectrometers or at synchrotron set-ups) of museum artefacts has been reviewed [6]. During the past few years, the *in-situ* μXRF analyses became an emerging field aiming to the same analytical performance with respect to laboratory analyses.

These, as well as other non-destructive techniques have to be further evolved towards the development of portable instrumentation. Portable instruments will offer the capability of performing analyses in-*situ* and on location, given the restrictions related to the permission to remove bulk materials for destructive analysis or even to transport objects to a laboratory for scientific examination. Our goal is to develop an innovative approach to survey, analyze, and identify treatment priorities for large collections of metal artefacts, quickly and effectively. The approach must consider the complementary application of scientific techniques, such as LIBS and μ-XRF, and their ability to work together to obtain controlled elemental analyses of each of the stratified layers consisting the surface of a metal artefact.

The paper outlines the design and integration of the compact and portable LIBS and μ-XRF, as well as the research involved in the optimization of the parameters and operating conditions for accurate and precise measurements of the chemical compositions of metal artefacts. Furthermore, the survey approach developed for large metals collections in order to identify the treatment priorities and representative sample for further scientific analyses of the collection is described for two museums in Greece and Jordan.

2 The innovation needed for the analyses of metal artefacts

The conservation of metals artefacts is complex given the varying degrees of corrosion phenomenon that may occur for a metal substrate under different burial conditions. The corrosion of a metal artefact prior to conservation treatment is dependent on the type of metal, burial environment, and handling / storage after excavation. The corrosion layers formed in burial conditions is the result of the electrochemical process between the metal substrate, electrolytic solution, and chemical species that exist in the burial environment. For this reason, the same type of metal artefact in different burial environments may have differing corrosion layers and degrees of corrosion, and the same is true for different metal alloys in the same burial environment. Furthermore, a metal artefact consists of different stratified layers of corrosion products with or without a metal substrate depending on the degree of corrosion. The goal of the conservator-restorer (C-R) is two-fold: to stabilize any remaining metal and to find the original surface or shape of the artefact, which contains important information concerning the technology and/or anthropomorphic use of the object. The search for the 'original surface' during cleaning by a C-R professional requires both in-depth probing and adequate knowledge in the theory of corrosion for each type of metal. However, prior to such investigative cleaning, it is important to determine more precisely using diagnostic techniques the chemical and mineralogical compositions of the metal artefact so as to ensure that important information is not lost during cleaning. Furthermore, there is a need for analytical techniques to be able to routinely and quickly analyze these stratified layers with minimum or no destruction to the artefact. Finally, it may be impossible to apply such routine diagnostic analyses to an entire collection of metal artefacts given its size – thus, a representative sample may need to be selected to identify the conservation problems and needs of the collection. How this representative sample is selected for further scientific analyses must also be addressed so as to ensure that the scientific results have meaning for the preservation of the collection.

The corrosion layers of a metal artefact are often hard and difficult to remove mechanically in a controlled manner using simple hand tools. Furthermore, the corrosion layers may be quite thick (up to many millimetres) before reaching the metal substrate. Thus, most scientific research of metals artefacts involves taking destructive cross-sections of the objects to determine the chemical and mineralogical compositions of both the metal substrate and its corrosion layers respectively. Such an approach is limiting as to how many artefacts may be sacrificed for such purposes, and in some countries is nearly impossible to apply given the need for official permissions. As a result, analytical techniques need to be designed to take minimum sample but at controlled locations and depths within the sample.

The application of LIBS suits well this purpose since it provides on-line in-depth analysis of the various layers of the studied surface by laser ablation of a minute amount of material (1-10 μm in depth and ~100 μm in diameter). On the other hand, μ-XRF offers non-destructively compositional information of the superficial layer. The combination of both these techniques allows for an integrated analytical study of both the outer surface as well as the stratigraphy of the corrosion layers, with minimum material loss. Such an innovative aspect would advance the in-*situ* analytical characterisation of metals collections. Furthermore, our research will have an impact in the field as to the analytical information that can be determined from metal objects in-*situ* by upgrading the following criteria:

Fast, so that a large number of objects may be analysed or a single object investigated at various locations.

Versatile, allowing to obtain average compositional information but also permitting local analysis of small microscopic areas.

Sensitive and multi-elemental on-line analysis, making possible the use of trace-element fingerprints.

During the first year of our project, which involves the documentation and monitoring of metals collections, three tasks were completed and necessary before an integrated approach could be applied for the analyses of large metals collections using the innovative analytical techniques:
- Developing a survey methodology and the survey of metals collections;
- Development of portable μ-XRF;
- Development of portable LIBS.

The development of the survey methodology has been described in an extended abstract given in the same proceedings [7]. The survey approach applied in two cases described below involves using a statistical methodology in assessing the technology and condition of a large sample of the objects.

3 The museum collections

Many museum collections in the Mediterranean region are located at the archaeological sites where the excavations took place. The archaeologists or curators are responsible for the care of both the archaeological site and excavated objects. The restoration of buildings and structures associated to the site often take precedence over the conservation / restoration of the objects stored in the museum since they are more visible to the public and monies are more easily raised (either private or public) for them than the objects. Furthermore, archaeologists often do not offer proper care and handling of the objects during excavations – so that when objects are removed from wet burial environment – they are allowed to dry out. To compound this problem, they are often stored inadequately, and it may be decades before any conservation treatment takes place. As a result, archaeological finds most sensitive to changes in the environment after excavation such as iron, copper, or silver alloy artefacts suffer a great deal. The best that can be hoped for is that the excavated metal artefacts are completely mineralized and contain no metal so that they will remain stable and not turn eventually to dust.

3.1 Copper alloy and iron collection at the Archaeological Museum of Ancient Messene

The metals collection at the archaeological museum at Ancient Messene in the Peloponnese Peninsula was chosen for study by the TEI, since it has not been investigated before and is typical of the problems mentioned above. With artefacts ranging from 369 BC to the sixth century AD, the collection covers 174 years of excavations including sculpture, building elements, pottery, and 5,000 metal artefacts – 13,000, including coins. Due to the large size of the metals collection, T.E.I. chose a representative sample of one thousand (1,000) artefacts of iron and copper alloys from the 5^{th} century BC to the 6^{th} century AD. Messene site average temperature and RH in summer 25.6 ºC and 59.2 % and in winter 10.8 ºC and 73.1 % respectively. The artefacts were separated into typological groups and documented according to type, description, dating, condition, and excavation context. A condition survey was conducted whereby data was collected for all variables described above using Excel tables with other important variables, such as burial environment, archaeological significance, and storage conditions.

T.E.I. also carried out a technological survey. Frequency tables were created whereby the same variables exist in the columns and rows, and each object is counted according to occurrence for each variable. The design of frequency tables used morphological characteristics and other technological features of the objects. Classification trees and pie charts were produced to show frequency of appearance and distribution of specific technological features for each category.

3.2 Copper alloy collection at the Museum of Umm Qais, Jordan

Umm Qais (Graeco-Roman town) situated 110 km north of Amman on a broad promontory 378 meters above sea level with a magnificent view over the Yarmouk river, the Golan Height, and Lake of Tiberias. Umm Qais is known as Gadara, one of the most brilliant ancient Greco-Roman cities of the Decapolis; and according to the Bible, the spot where Jesus cast out the Devil from two demoniacs (mad men) into a herd of pigs (Mathew 8;28-34). Umm Qais site average temperature in summer 26-30 ºC and 10-14 ºC in winter, with annual RH 50-70%.

What are left of the ancient city remains are temples, theatres, public baths, a chariot-race hippodrome, and an underground mausoleum. Currently, the museum houses 51 copper alloy artefacts of different periods, Roman, Byzantine and Islamic. Artefacts were found in the baths, tombs, and the Mausoleum. Condition and technological surveys were carried out by RSS using the same methodology as for the TEI. The metals collection at Umm Qais like Ancient Messene has never undergone conservation treatment.

4 The development of a portable micro X-ray fluorescence spectrometer

The Demokritos portable micro-XRF spectrometer has been developed to fulfill certain analytical needs raised from the limited performance of conventional milli-beam XRF spectrometers in the characterization of corroded surfaces of various types of metal alloys. The surface or in-depth local distribution of metals corrosion products is considered to be in general very inhomogeneous with complex chemical and metallurgical structure. Therefore, the analytical probe should be able to provide spatially resolved analytical information (in the range of few tens of micrometers), improved analytical range (including light elements) and an automatic scanning capability in order to be able to identify local inhomogeneities. These basic requirements, together with the need for performing analyses in-situ, have actually determined the specifications of the individual microXRF instrumentation components. The spectrometer head (Fig. 1) consists of an optical element (polycapillary lens, IfG), a laser pointer and a color CCD camera for inspecting the individual analysis spot. The selected type of polycapillary lens exhibits optimum performance in the transmission of low and higher X-Ray energies (allowing the efficient excitation of low and medium atomic number elements) and minimum halo effect. The spectrometer is further composed by a Rh-anode air cooled X-ray tube and a Silicon drift detector (Rontec) with associated electronics that can process high input counts rates, without significant worsening of the detector resolution and dead time losses. Three different stepping motors, coupled with the spectrometer head, allow its three-dimensional movement, setting precisely the analysis spot at the focal distance of the polycapillary lens and providing the possibility for advanced elemental mapping studies. The spatial resolution of the microXRF set-up was measured in a line scan with a 50 um Cu wire and was found to be equal to 78 μm for 8 keV characteristic X-rays (Fig. 2). A typical spectrum of a standard reference bronze alloy obtained in a counting time of 5 sec is shown in Figure 3.

Figure 1: The μ-XRF of "Demokritos"

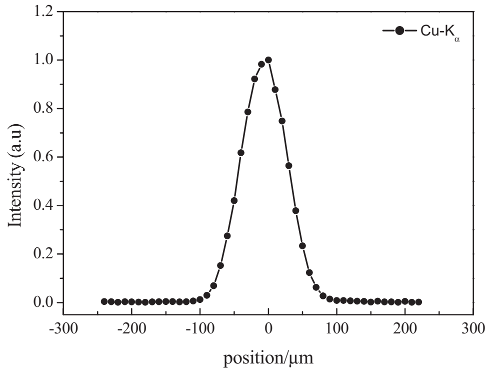


Figure 2: Wire scan of a 50 μm Cu wire

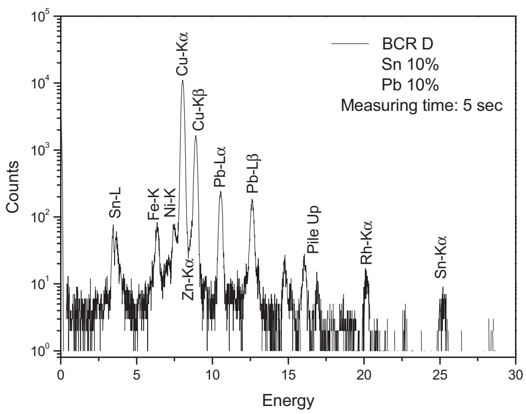


Figure 3: BCR_D spectrum

5 The development of a portable LIBS instrument

In response to the need for portability the development of a compact LIBS instrument was undertaken by IESL-FORTH. The outcome is LMNTII (el-em-ent-two), a portable hand-held system, shown in Figure 4. The unit comprises a compact Q-switched Nd:YAG laser (and its power supply) producing 8 ns pulses at 1064 nm with energy up to 17 mJ and a small spectrograph equipped with a CCD detector, featuring spectral resolution of 1 nm and covering a spectral range between 300-650 nm. Appropriate optics are used to focus the beam down to a spot of diameter around 100 μm, while an optical fiber is used to collect the plasma emission into the spectrograph. The whole system weighs less than 5 kg and can be transported in a small case. It requires regular power (but has the option of battery operation). The detector is USB controlled and operated through a laptop PC. In a typical analysis the probe head is positioned in contact with the object ensuring proper focusing of the laser beam on the object's surface and a single laser pulse is delivered by pressing a trigger button. The plasma emission yields a clean LIB spectrum that is displayed on the computer. Figure 5 shows a spectrum obtained from a sample of brass. Characteristic emission lines from copper (Cu) and zinc (Zn) are marked.

Figure 4: Picture of the portable LIBS unit (LMNT-II) featuring the probe-head, which contains laser head and focusing optics, and the main unit, which houses the laser power supply and the detector

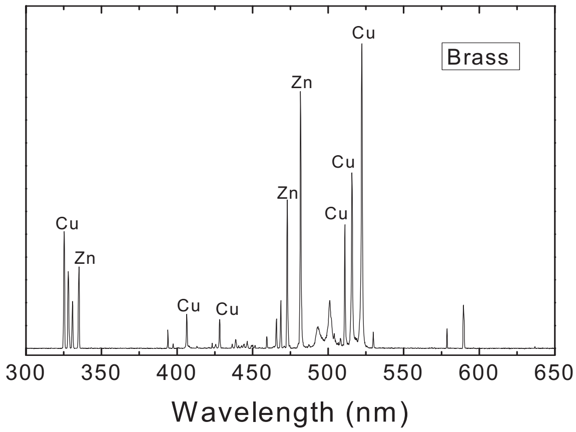


Figure 5: LIB spectrum from brass

6 The survey of the collections and some analytical results

The basic problem of the metals collections at Ancient Messene, Greece and Umm Qais, Jordan is that their value in terms of ancient metallurgical techniques and archaeological significance are unknown. Furthermore, the condition of the artefacts and their need for treatment has been neglected. To compound this, the storage conditions are uncontrolled, resulting in an indoor environment with wide temperature and RH fluctuations during the year. Our technological and condition surveys were essential in order to understand the following:

- the characteristic technological features of each specific type;
- the metallurgical techniques;
- the significance and the value of the collections;
- the treatment priorities of the collections;
- to select a representative sample for further diagnostic analysis.

While, certain diagnostic techniques need only be applied to a representative sample in order to obtain a clear picture of the conservation problems and needs, other techniques, such as X-ray radiography are an essential first step and need to be applied to all artefacts.

6.1 Archaeological Museum of Ancient Messene

A portable X-ray radiography was used to reveal hidden clues as to the methods of manufacturing, decorative detail, as well as the overall condition of the artefacts [8]. All the selected artefacts, nearly 1000 objects, were examined by this portable system. In the case of Ancient Messene, the iron artefacts from the collection exhibited clear signs of active corrosion (e.g., presence of akageneite and detachment of pieces known as spalling). However, only through the application of portable X-ray Radiography could the amount of metal remaining as well as the initial shape or form of the artefact be determined.

For the copper alloy artefacts, X-ray radiography was able to distinguish between the cast and/or hammered objects as well as surface decoration and features, not always visible due to the presence of thick corrosion layers. Furthermore, the analysis determined the actual condition of the objects, when the extent of internal cracks and fissures were hidden underneath the corrosion products.

From our technological and condition surveys (including radiographic analysis), 51 copper alloy objects were selected as representing all the characteristic types of the collection for further materials analyses using portable XRF, XRD and LIBS. Iron alloy artefacts were not included in this selection, since it is common knowledge that for this period only wrought iron was used for such objects, and the corrosion products for this type of metal is well documented in the literature [9].

A preliminary analysis of these artefacts was conducted using a portable milli-beam XRF system developed by Demokritos NCSR, in order to obtain quantitative results for the composition of the alloy (after removing the corrosion layer from a small area) and qualitative information about the composition of the surface layers of the artefacts (plating and corrosion products). In a next stage, the μXRF and LIBS analyses will be conducted. By this way a direct comparison between the two excitation modes of XRF systems will be feasible aimed to evaluate and access the analytical performance of the μXRF towards: 1) the characterization of metal corrosion products and 2) accurate quantitative analysis. The example of the mirrors is presented, in order to enlighten the applied methodology of our surveying approach in terms of technological characteristics and the condition of this group.

From the classification tree, most of the mirrors are circular in shape, do not have a handle, and can be divided into characteristic subgroups according to their profile, simple flat, raised rims, and thickened rims. Also, 60% of the mirrors are not plated, whereas the 40% are plated, probably with tin, and 60% of the mirror are simple and do not have any kind of surface decoration. From the condition survey, the group of mirrors, 6 objects need to be urgently treated since they exhibit signs of active corrosion products, 4 objects could benefit from treatment since they exhibit stable corrosion products.

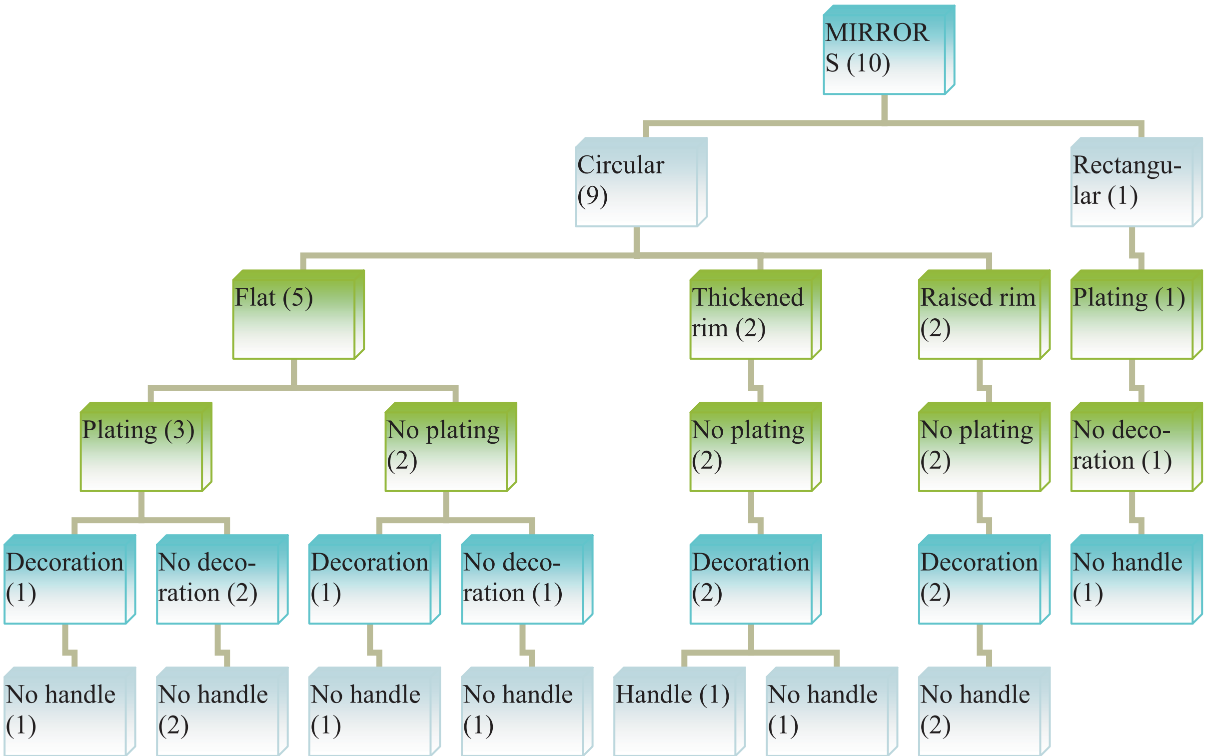
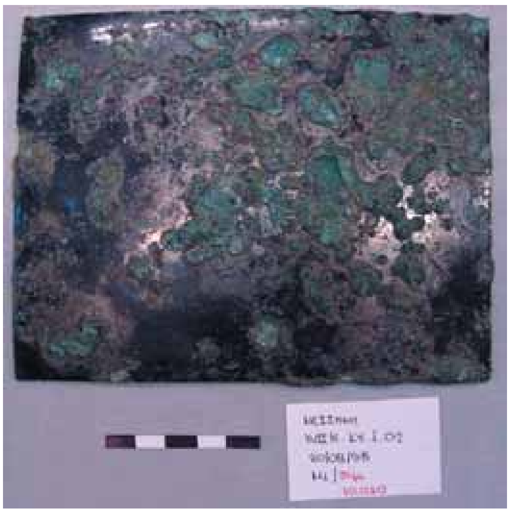


Figure 6: Classification tree of the technological profile of the mirrors

Finally, examples of the results of X-ray radiography and XRF analysis are shown in Figures 7-8, accompanied by Table 1 presenting the XRF results regarding the manufacture alloy.

Table 1: XRF results of mirror in Figure 7

Fe (%)	Cu (%)	Zn (%)	As (%)	Sn (%)	Sb (%)	Pb (%)
0.1 ± 0.01	70.6 ± 0.3	–	< 0.03	26 ± 0.3	< 0.21	3.4 ± 0.1



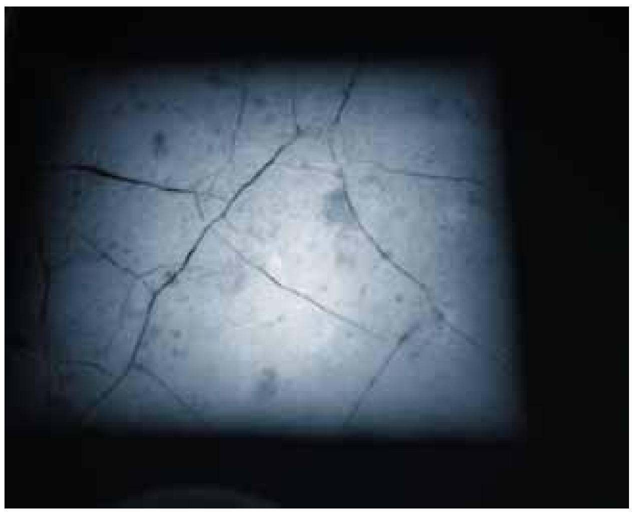


Figure 7: Rectangular mirror, tin-plated (2nd c. B.C.) Figure 8: X-Radiography (85 kV, 30 mAs, 3 sec). The radiograph depicts the cast structure, the extent and thickness of cracks and fissures. The light areas are probably lead.

6.2 Museum of Umm Qais, Jordan

Umm Qais site consists of limited metals collection, but excavations are still underway. The RSS team chose to analyze the copper alloy objects from the Islamic period, since it represents wide range of similar collections in the Hashemite Kingdom of Jordan. Most of the artefacts were found in the bath area, and the rest in the tombs and underground Mausoleum.

The condition survey at Umm Qais museum to identify treatment priorities identified that 47% of the copper alloy artefacts are in need of urgent treatment, while 53% can benefit from this treatment. As for the amount of metal remaining: 10% have no metal, 29% have little metal remaining, and 61% have substantial metal core. Also, 43% have signs of active corrosion. It is worth mentioning that, 37% were excavated from wet soil burial environment.

Preliminary diagnostic testing was undertaken for 10 copper alloy artefacts at Umm Qais Museum using visual observation, chemical analysis using SEM with EDX for the base metal and oxide layers.

Figure 9: A copper alloy jug from the Umayyad period, with a large red stain and active corrosion at the base of the jug

Table 2: SEM-EDX results

Element	Cu	Fe	Si	Zn	Sn	Pb
Wt%	75.58	0.28	0.24	0.82	8.19	14.90

6.3 LIBS Analysis of Bronze Coupons

NILES is working on constructing calibration curves using certified bronze coupons for Zn, Pb, and Sn in bronze. Nd-YAG laser delivering laser light pulses of 100 mJ pulse energy, of 6 ns pulse duration at 1064 nm wavelength was applied. The laser was focused onto the sample surface and the emitted light from the produced plasma was analysed via a modern echelle-spectrometer coupled to an ICCD camera. The obtained plot of the concentration versus the emission line intensity represents the calibration line of the relevant element. Knowing the intensity of the same emission line in any other bronze sample leads to the knowledge of the element concentration in such sample. Figure 10 shows the obtained calibration lines and the values of the Zn, Pb, and Sn concentrations in the bronze coupons used to simulate bronze metallic artefacts. The obtained concentrations are in very good agreement with the listed values for the coupons composition. This means that the technique can be reliably used in the elemental analysis of any real bronze artefact.

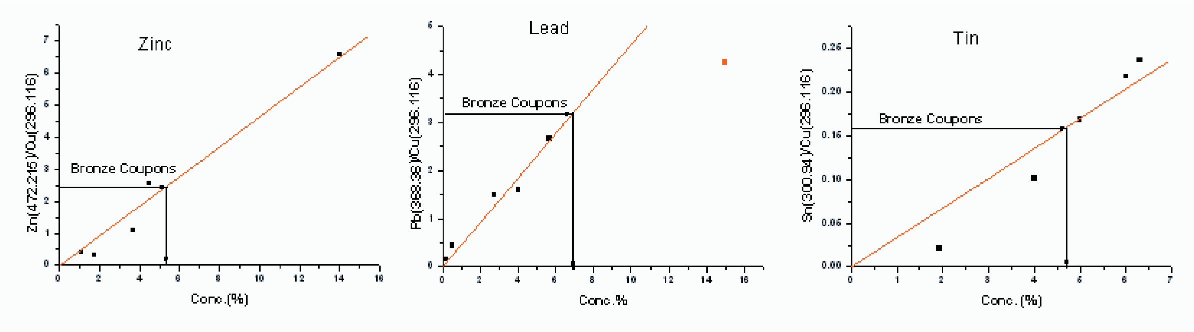


Figure 10: Calibration lines of Zn, Pb, and Sn. The arrows indicate the intensities of the elements emission lines in the bronze coupons and the corresponding concentration

7 Discussion – future tasks

The study of the radiographs and the XRF results for the copper alloy mirrors at ancient Messene indicate that all the mirrors were made by casting, characteristic in the radiographs by the porosity, the thickness variations, and a coarse granular appearance or texture that is usually present for cast objects. Furthermore, the light areas are usually indicative of the presence of lead in the metal and the dark areas show where the metal is thinner. The extent and the thickness of cracks and fissures are clearly identified. All the mirrors dated from the 2nd c. B.C. are high tin bronzes with an elaboration of the surface enriched in tin. All the mirrors dated from the 4th and 3rd c. B.C. are bronzes, presenting tin from 6.6-12.3%. Lead is present almost in all mirrors, ranging ~ 3.5-5.1%.

The preliminary scientific investigation for the copper alloy objects at Umm Qais revealed that the jugs, bracelets, and rings consist either of pure copper, brass, or bronze. All artefacts showed signs of active corrosion, with some areas displaying crevice and/or pitting corrosion. As stated above the artefacts are typically left to dry out after excavation and stored in uncontrolled conditions.

The experimental results obtained adopting the LIBS technique and the development of the portable system show that in-*situ* applications of LIBS are feasible. So, elemental analysis of metal artefacts in museums using LIBS will help in monitoring any changes due to the environmental effects to support conservation and restoration procedures.

The future tasks are to analyze a representative sample of copper alloy artefacts from both sites using the portable microXRF and LIBS techniques so as to obtain further information concerning the technology and condition of the artefacts.

8 Conclusions

European Dimension: The results of the project offer a cost effective approach to identifying the conservation problems and needs of a metals collection using state-of-art portable diagnostic techniques.

Innovation and Originality: The condition survey methodology developed for this project is original and allows for quick and easy conservation assessment of large collections using statistics. The μXRF technique has not been evaluated up to now concerning its possibilities to identify various metal corrosion products. This effort would be an important task within PROMET together with the development of reliable quantitative algorithms.

Finally, the development of portable and reliable LIBS and μXRF instrumentation specifically optimized for the analysis of metal corrosion layers and substrates, as well as their complementary application for a thorough investigation of depth profiling of objects are among the innovative features of this project. It is expected to introduce a new approach for the scientific analysis of metal collections in-*situ* and thus provide a clearer picture of the conservation problems and needs.

Impacts: The achieved results for this project can easily be applied to any museum setting world-wide due to the portability of the instruments developed and the methodology is easily transferable.

9 European project details

PROMET, Contract No. 509126, Developing new analytical techniques and material for monitoring and protecting metal artefacts from the Mediterranean region, Co-ordinator: Vasilike Argyropoulos, The Department of Conservation of Antiquities & Works of Art, Technological Educational Institute of Athens (T.E.I. of Athens), Ag. Spyridonos, Aigaleo – Greece 12210, Email: bessie@teiath.gr .

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Corrosion of lead and lead-tin alloys of organ pipes in Europe

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Key words: organ pipe, corrosion, lead, organic acid

Abstract
The European heritage of the organ is preserved in numerous historical instruments, many of them located in eastern part of Europe. One major threat to this heritage is the indoor atmospheric corrosion of lead and lead-tin alloys of organ pipes.

The COLLAPSE (Corrosion of Lead and Lead-Tin Alloys of Organ Pipes in Europe) project is a research project supported by the European Commission under the Fifth Framework Programme, Key Action "The City of Tomorrow and Culture Heritage".

The project objectives are to define methods, products and conservation strategies in order to combat the pipe corrosion.

Field studies have been performed at selected corroded and not corroded organs in Italy, the Netherlands, Belgium and Germany. The field studies include documentation of the organs, analysing corroded pipe samples, sampling and analysing the environment in the organs and in the churches. Laboratory research has been performed to investigate the corrosivity of environmental factors and substances found in the field studies. A strong corrosion factor being found is the emission of organic acids, especially acetic acid, from the wooden parts in the organ. Polyvinyl acetate glue (white glue), often used when restoring or building organs, is known to emit acetic acid and is also a corrosion factor.

A method has been developed to clean corroded pipes. Cleaning is done primarily to decrease the rate of corrosion by removing soluble corrosive salts from the surface.

The developed conservation strategies have been applied in a case study using the historical Stellwagen organ in St. Jakobi church, Lübeck, Germany, severely affected by corrosion.

Valves have been installed in the organ wind system in order to evacuate the accumulated organic acids before start playing.

1 Introduction

The pipe organ and its music are important parts of the cultural heritage of Europe. They have been developed in the context of western polyphony. The organ reflects European traditions, thinking and general history. It brings together wood and metal craftsmanship, knowledge in mechanics and pneumatics. All these skills are combined to a high level of artistry in order to create music. During many centuries the organ has represented high tech and its development has mirrored the technical, social and economical development in society in different regions in Europe. An organ landscape has been created, implying many common traits but also fascinating differences in construction, style and sound. It makes the organ a central and indispensable part of our European sounding cultural heritage.

The number of historical organs still extant in Europe is surprisingly high, not least in Eastern Europe organ heritage found in all countries of Europe includes more than 10,000 historically valuable organs.

One major threat to these instruments is the corrosion of lead and lead-tin alloys of the metal pipes, constituting the central sounding part of the organ.

In the mid 1990's a heavy corrosion attack was discovered inside the Principal 16' prospect pipes in the famous Stellwagen organ in St. Jakobi church in Lübeck.

The corrosion had begun to cause cracks and holes in some of the pipes and something had to be done in order to save these invaluable and wonderful sounding pipes from 1467.

The questions were:
Why did these old pipes suddenly start to corrode during the last decades?
How to treat the corroded pipes and to keep them from corroding further?

These questions were the point of departure for the COLLAPSE (Corrosion of Lead and Lead-Tin Alloys of Organ Pipes in Europe) project. The COLLAPSE project objectives have been to define relevant methods and products as well as to create conservation strategies in order to combat the corrosion of lead and lead-tin alloy organ pipes through (i) field studies and laboratory experiments identifying the factors which cause indoor atmospheric corrosion of lead-tin alloy organ pipes in order to avoid or impede corrosive environments, (ii) development of methods to clean, protect and preserve already corroded pipes to keep them from corroding further and (iii) application of the recommended conservation strategies in a case study using the historical Stellwagen organ in St. Jakobi church, Lübeck, severely affected by corrosion.

2 Methodology

The field studies have included selecting and studying organs affected by corrosion and comparing them with organs in similar locations not being affected by corrosion.

Field studies have been performed at the following organs:
Basilica di S. Maria di Collemaggio, L'Aquila, Italy, second half of 17th century (corroded).
Church of Madonna di Campagna, Ponte in Valtellina, Italy, 1518 (not corroded).
Groene of Willibrorduskerk, Oegstgeest, the Netherlands, 1976 (corroded).
Waalse kerk, Amsterdam, the Netherlands, 1734 (not corroded).
The Koninklijk Conservatory, Brussels, Belgium, 1880 (corroded).
The Jezuietenhuis, Heverlee, Belgium, 1880 (not corroded).
The Stellwagen organ in St. Jakobi church, Lübeck, Germany, 1467 (corroded).

The field studies included documentation of pipe corrosion damages, room and organ condition. Microstructure and chemical analysis of corroded and non-corroded pipe metal was performed and also analysis of corrosion products.

Gas analysis of the church environment and the organ wind supply has been performed.

Temperature and relative humidity have been logged during more than one year in positions close to the pipes and close to the organ wind inlet. These positions have been selected in order to detect the possibility for condensation in the pipes.

Metal samples that mimic the material used in historical organ pipes have been exposed inside the organs, in the pallet box, with the intention to provide information on the corrosivity of the environment in the field study instruments.

Laboratory experiments have been performed under controlled environmental conditions in order to measure the corrosion effect on pipe metal of environmental factors and substances found in the field studies.

3 Results and discussion

In the field studies there were several positions on the pipes where corrosion could be found:

(1) On the outside of the pipe where the metal is in contact with the pipe support or on the foot tip where the pipe is standing on the toeboard. The reason for this is well-known. It is the organic acids in the wood being in direct contact with the metal causing the corrosion.

(2) Inside the pipe foot. This is the typical corrosion damage being in focus for the COLLAPSE project. The corrosion starts in the lower part of the foot and moves gradually upwards in the pipe towards the mouth area. If nothing is done, there will be cracks and finally holes in the pipe foot wall. If the corrosion reaches the mouth the sound properties will gradually change and finally the pipe will be silent. This is of course very serious because the historical sound quality will be lost and the sounding cultural heritage will be gone forever.

(3) The blocks in reed pipes. This is a common location for corrosion damage in 19th century organs.

In spite of the fact that some of the field study organs were selected as non-corroded, they appeared to contain some corrosion.

High concentrations of acetic acid and also formic acid and aldehydes were detected in the organ wind in the corroded field study organs [1].

Laboratory research has shown that acetic acid and formic acid also in very low concentrations is very corrosive to lead [2, 3]. Inorganic air pollutants from combustion, e.g. SO_2 and NO_2, do not seem to be the causes for the corrosion of organ pipes [4].

The organic acids are emitted from the wooden parts in the organ (in the windtrunks and in the windchests). Especially oak is known to emit large amounts of organic acids and especially acetic acid.

There are two different situations when the organic acids could enter into the pipe foot: (i) the "sounding" condition when the pipe is played, the wind containing the acids will flow through the foot and (ii) the "silent" condition when the pipe is not played, the organic acids emitted from the wall in the toeboard hole under the pipe will slowly enter into the foot through the foot hole. It is hard to estimate how much the first or the second situation will contribute to the corrosion situation but it is probably a combination of both. However, the fact that a pipe spends most of its time not being played and also that several of the silent facade pipes (there are 4 decoration pipes in the facade never being played) in the Stellwagen organ in St. Jakobi church are very affected by corrosion indicates that the "silent" condition may give a major contribution to the corrosion attack. There were holes drilled in the toeboard also under the silent pipes.

A question is how old organs could survive several hundred years without corrosion problems when oak has always been used for making windchests and windtrunks. We did find historic documents from the 17^{th} and 18^{th} centuries describing frequent corrosion problems and also that the pipes in a new organ could be completely destroyed by corrosion in less than 30 years, especially if the pipes were made of high lead composition metal.

Today there is a danger if new wood is introduced into an old organ during restoration or repair work. In the Stellwagen organ in St. Jakobi church the toeboards are made of oak. This oak is not old but was installed during the last restoration of the organ, 1977-78. Many wooden parts made of oak in the windchests and also new windtrunks of oak were installed at this restoration.

Another observation in this organ supporting the assumption that the organic acids are the major problem is that the pipe feet with the smaller volumes are more corroded than the larger ones. The reason is that the concentration of acids will reach higher levels in the smaller pipe feet volumes.

Knowing that acetic acid creates lead corrosion, the use of polyvinyl acetate glue, often called white glue, in the organ can be another factor creating corrosion. There are many different types of white glue but they all emit acetic acid. Some of them emit when they are fresh and others emit acetic acid when they are ageing. Some of them release large quantities of acetic acid. This modern glue has been used by most organbuilders since the beginning of the 1960's.

The composition of the pipe metal is an important factor having an influence on the corrosion situation. In a corrosive environment, metal containing less than about 1% tin, like the corroded pipes in St. Jakobi, is very sensitive to corrosion, but a few percents of tin in the alloy make the metal more corrosion-resistant [5].

When repairing a corroded pipe the same alloy as the original pipe metal alloy should be used. Using an alloy containing more tin for replacement of a corroded and damaged pipe foot tip can result in a corrosion attack above the replaced material closer to the sensitive mouth area.

The temperature and especially the humidity will influence the corrosion situation.

The field studies have shown that the concentrations of organic acids in the organ wind system depend on temperature and humidity. The emissions from wood were about 5 times higher during summer compared to wintertime in the Stellwagen organ [1].

Condensation phenomena inside the pipe foot has often been suggested as the reason for the corrosion. When playing the organ, a condensation situation could occur if warm air from the wind inlet would be transported through the wind system, enter into the foot and come in contact with the cold metal surface inside the pipe foot.

No condensation situations could be detected in the measuring period in the field study instruments. However, this does not prove that condensation inside the pipe foot could not occur. It would certainly speed up a corrosion process but we do not think the condensation to be the key factor creating the pipe corrosion.

The development of methods to clean the corroded pipe metal surface has been a part of the project. Investigation if water leaching is beneficial from a corrosion point of view has been performed [2]. A method has been developed to remove soluble corrosive salts from the corroded pipe surface. The insoluble corrosion products (e.g. lead white) are not to be removed.

The corroded Principal 16’ façade pipes in St. Jakobi church, Lübeck, were dismantled, cleaned and repaired. The pipes are now back in the organ.

The cleaning of the pipes will not help the corrosion situation if the environment is still corrosive. Therefore it was very important to impede the corrosive environment in the Stellwagen organ. The toeboards were exchanged using a type of wood with lower emissions.

New developed valves were installed in the organ wind system in order to automatically ventilate the organ before it starts playing so the wind containing accumulated organic acids will be evacuated.

4 Conclusions

The European heritage of the organ is preserved in numerous (more than 10 000) historical instruments, many of them located in eastern part of Europe. One major threat to this heritage is the indoor atmospheric corrosion of lead and lead-tin alloys of organ pipes.

A strong corrosion factor is the emission of organic acids, especially acetic acid, from the wooden parts in the organ. Polyvinyl acetate glue (white glue), often used when restoring or building organs, is known to emit acetic acid and is also a corrosion factor.

The results and recommendations from COLLAPSE will create a new approach among organbuilders when restoring or repairing an historical organ.

It is important not to create a corrosive environment when introducing new wood when repairing or restoring an old organ, especially if the instrument contains high lead alloy pipes.
The wood should not be fresh but it should be stored for a long time.

Avoid using oakwood, especially for the toeboards (even if it is historically correct), but use wood with lower emissions of organic acids.

Avoid the use of polyvinyl acetate glue (white glue).
When repairing a corroded pipe use the same alloy as the original pipe metal alloy.

The recommended actions to avoid or impede a corrosive environment including cleaning of corroded pipes have been applied in the Stellwagen organ in St. Jakobi church, Lübeck.

The results from COLLAPSE have generated necessary input and an important point of departure for the new project SENSORGAN (FP6, contract no. 022695). The overall objective for SENSORGAN is to develop sensors for detection of harmful environments for pipe organs, thereby providing a tool to detect and assess environments corrosive to organ pipes.

5 Acknowledgements

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Radiofrequency identification for movable heritage management

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Key words: radiofrequency, traceability, security, standards, documentation, artwork

1 Introduction

Nowadays several conditions are affecting movable heritage objects management. By one hand there is a high mobility index affecting these objects (transportation, warehouses, exhibitions,…), by the other in most cases there is no accessible information concerning to heritage object, and hence a growing non-security environment arise close to the museums, investors and artists.

This paper will introduce Radiofrequency Identification (RFID) as the most efficient technology to ensure *traceability* and security for any kind of heritage object. This goal will be achieved by applying all the RFID benefits to the heritage object *documentation process.*

2 About RFID

Radiofrequency Identification is an automatic data collection technology (ADC) which exchanges data wirelessly. Its basic elements are:

- The tag (or *smart label*), a kind of label that is applied to an object or document and contain a chip and an antenna, allowing both storage and transmission of information, respectively.
- The readers: devices that use RF signals to extract the information of the tags that are within its read and frequency range. Data recovery is done automatically. After receiving and processing the information, the reader transmits it to the corporate information systems (see figure 1).

Figure 1: A RFID reader (left) and its antenna

One of the most important issues in RFID today is the adoption of standards. ISO/IEC and EPCglobal are the two main standardization organisms for RFID regulations.

- ISO/IEC is a joint venture formed by the International Organization for Standardization (the world's largest developer of international standards, worldwide accepted and used) [1] and the International Electrotechnical Commission (leading global organization that prepares and publishes international standards for all electrical, electronic and related technologies) [2]. ISO/IEC provides technical regulations for both people and objects traceability.

- "EPCglobal is a joint venture between EAN International and the Uniform Code Council (UCC) entrusted by industry to establish and support the Electronic Product Code NetworkTM as the global standard for immediate, automatic, and accurate identification of any item in the supply chain of any company, in any industry, anywhere in the world is the organization" [3]. The aim of EPCglobal is to boost the adoption of the Electronic Product CodeTM (EPC) as the next generation of product identification, given that, unlike current barcode systems, the EPC – among other advantages – has been created with a data structure of 96 bits capable of uniquely identify all the objects (items, cases, pallets, locations, etc.) in the supply chain.

Another relevant matter is the selection of the frequency band, that may determine aspects such as the read distance (the distance from the reader to the tag), the speed reading or the tag size. The frequencies more often used are:

- High frequency (13.56 MHz), read distance up to 3 metres, medium speed reading and small size of tags.
- UHF (between 859 and 960 MHz, depending on the zone), with read distances up to 20 metres, higher speed reading and bigger size of tags.

The adoption of RFID technology (although it has more than 50 years of history) is currently growing fast due to the implementation of the standards above mentioned, the equipment improvement and falling implementation costs.

3 Traceability and RFID for heritage objects

We understand traceability as the ability to track an artwork through its complete life cycle. In other words, the capability to:

- identify
- register
- and transmit the art information anytime and anywhere.

The tracking solutions based on RFID provide this visibility through the whole art chain. The contributions of this technology to heritage objects traceability are directly related to the label (TAG) features:

- Each tag has a unique serial number which allows individual and unrepeatable identification of the art object worldwide.
- Additional data store area, which drastically enhances the capabilities of current marking systems, such as barcodes, being able to register all the processes that affects the heritage object life cycle.

- No line of sight is required to get the data from the tag. This permits the tag to be embedded and so be able to work in harsh environments (high temperatures, contact with chemical elements, ...).
- Intrinsic security elements and encryption possibilities that made the tags hardly difficult to counterfeit.
- Availability of sensor devices: a specific kind of these smart labels, called active tags, can bring embedded temperature or humidity sensors, that permit complete, automatic monitoring of these parameters wherever the art object is found. This warranties a complete tracking of transportation and warehousing.
- Information availability anywhere, anytime: RFID offers us the possibility to interact with the tags through the most common devices currently in the market, like mobile phones or PDA's.

These fortresses of the technology bring us to conclude that RFID is a useful and secure tracking technology for the management of cultural heritage objects. But many problems may arise so far when trying to mark directly the artwork: different types of art objects, difficulties in their manipulation, preserve requirements or even the existence of protected rights that impede any transformation on the objects.

For this reason, and in order to develop a standard useful for all types of art objects, our proposal – at this point – is not to mark the object itself (although Saident continues investigating different possibilities of embedded tags – see figure 2) but the documentation related to it. And this will be executed in two steps: firstly we have to create a documentation process suitable for any existing work of art, and secondly, once the different steps of the process have been defined, we will apply the RFID benefits on each of them.

This project will be carried out in close collaboration by Saident and AICOA (Archivo Internacional Central de Obras de Arte – Central International Archive of Artworks), a European based organisation specialised in the documentation of artworks.

Figure 2: RFID tag embedded

4 AICOA project. How to apply RFID-based traceability to the world of art

AICOA is the first international archive specialized in documenting and registering Artworks (pictures, photographs, jewels, sculptures, digital art, …). AICOA's objectives are to promote the cooperation within the art world, watching for the quality of its documentation and protecting and guarding the information in order to give full warranties to authors, gallery owners, museums, private collectors and the rest of professionals of this world [4].

AICOA operates in Spain, Italy, France, Portugal and Andorra. In each of these countries there is a national representative who gives all the services to the art sector professionals. Oncoming countries soon integrated in AICOA are: The Netherlands, Belgium, Luxemburg, United States, Mexico, Argentina, Uruguay, …

These are the main processes of the AICOA operations model:

- Reception of the artwork
- Systematic description and documentation of the artwork in the DOA – *Description of Artwork* document
- Registry, archive and digital custody of the DOA and the rest of documents related to the artwork (authorship certificates, reports, brochures, …)
- Issuing of a passport guide that will track the artwork through its life cycle, adding information regarding exhibitions, registers and movements (transport, customs, …)
- On-line consultation (AICOA Intranet)
- Reporting and certification of the registered artworks.

These processes can be summarized in the three basic steps of traceability: identification, registering and information of the artwork.

4.1 Identification of the art object

In this step RFID tags are attached to the DOA document (see figure 3) and the passport guide (see figure 4).

The DOA document includes the following information: artwork code (GS1 standard), authorship declaration and experts certifications, technical features, different views of the pictures, public and confidential information.

The information registered in the tag is: serial unique number (ID unique), GS1 artwork code (Num. DOA), author's name and title of the artwork. The standard applied is ISO/IEC 15693:2004 (Information Technology – Automatic Identification and Data Capture Techniques – RFID for item Management – Unique identification of RF tags), and the frequency used HF 13,56 MHz.


AICOA

DESCRIPCIÓN DEL OBJETO DE ARTE PARA EL REGISTRO EN AICOA

Datos del registro

Fecha del registro: 24/8/2005

Tipo de registro: Unitario

Subtipo: Pintura

FICHA TÉCNICA DEL OBJETO DE ARTE

Título: ESTADOS COMPLEMENTARIOS 016

Técnica: MIXTA

Soporte: LIENZO

Época, corriente estilística: —

DECLARACIONES DE AUTORÍA

Nombre o pseudónimo: REY SENDÓN, PABLO

Firma artística

Firma legal

DECLARACIÓN DE REGISTRO

MUESTRA

SAMPLE

Figure 3: Cover of DOA document

Passport Guide with RFID tag ISO15693 enclosed, although adoption of e-passport technology (ISO/IEC 14443 – Identification cards – Contact less integrated circuit(s) cards – Proximity cards) is being studied, in order to share advantages when implemented in the very near future.

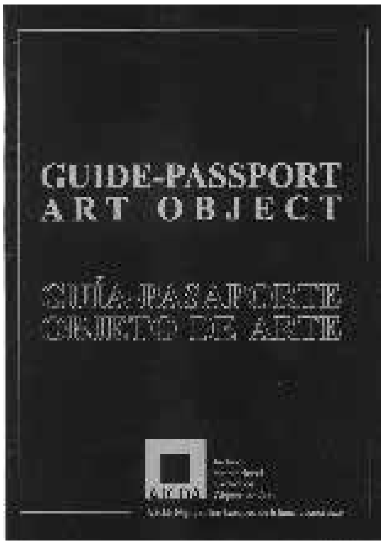

Figure 4: Cover of Passport document

The information on the different tags is registered through a RFID reader/writer ISO 15693 (see figure 5), and the frequency HF 13.56 MHz.

Figure 5: Tag and reader/writer

4.2 Registering and archive

All the documentation above mentioned must be kept in a high-security environment, in order to maintain its privacy. For this reason, AICOA's archive is adopting a RFID-based security system, with access control through a RFID arc and smart shelves with embedded antennas and RFID readers connected to the corporate application (ERP). Services soon offered will be:

- Localization: as you type the number of the desired folder in the computer, the solution gives you the position of that folder.
- Permanent inventory: the solution is in continuous reading mode, giving on-line information of all the documents archived in the shelves.
- Alarms: the solution is able to generate an alarm if one of the permanent inventories detects the missing of a folder.

4.3 Information transmission

The third step of the AICOA traceability process is covered by the AICOA central server and transactional website (see figure 6). Through the AICOA information data base, the users have remote access to the information of the artworks and the possibility (if registered) to update it on-line with additional data regarding participation in exhibitions, awards, restoration activities, artwork lending, incidents, … All this data is checked by AICOA before approval. Reports and certifications can be issued as well on-line (useful for transport or insurance companies).

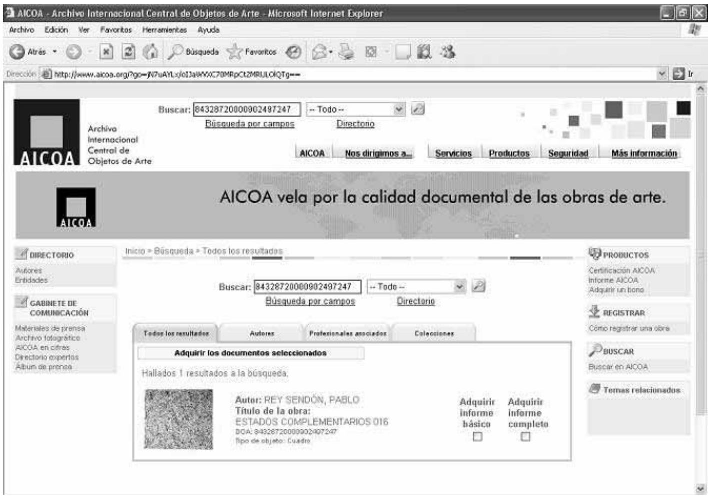

Figure 6: Search results screen of the AICOA Intranet

In a near future, and with the objective of improve and widen the international accessibility to all this information, is being studied the adoption of EPCglobal standards and its worldwide network, although we will have to wait until EPC create a standard for HF (the only frequency adopted so far is UHF). See how EPC Network works in [5].

5 Conclusions

Traceability is synonymous of security in the management of movable heritage objects, and Radiofrequency Identification Technology (RFID) is the best way to assure it.

The optimum traceability will be achieved when it is possible to mark each heritage object with a RFID label (tag). Provided the enormous casuistic existing and the need to study the best way (if possible) to attach a tag on each kind of them, this paper presents an alternative approach: tags (and so RFID processes) must be applied not to the heritage object but to the documentation that must accompany it.

So nowadays the absolute need is to develop a procedure that makes possible the documentation, registering and consultation of all types of heritage objects existing. A procedure that assures complete, appropriate standardization, traceability and security. This is the main goal of the AICOA's project.

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A new non-contact fingerprinting method for the identification and protection of objects of art and cultural heritage against theft and illegal trafficking

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[5] University of Southampton, Great Britain
[6] Ormylia Art Diagnostic Centre, Greece

Keywords: colour, fingerprint, identification, marking, roughness, theft, tracking and tracing, trafficking

1 Introduction

When a head of state or minister signs a cultural exchange agreement with a colleague from another nation, a collective shudder goes up the spines of the conservators and curators of museums, and collections of art and cultural heritage in those respective countries. It is not that they are against cultural exchange. Far from it, the opportunity to share collections and experience with other audiences, and to work with colleagues abroad is welcomed by all. Since the Treaty of Maastricht (1992), it has been, in fact, official European Community policy to encourage cultural exchange in all fields and at all levels to promote more cohesiveness and understanding within the community, as well as with third nations. This has resulted in, among others, several successful programmes aimed at supporting cultural heritage, including the Raphaël programme, and more recently and still current, the Culture 2000 programme. A common denominator of these programmes, and European cultural heritage policy in general, is the exchange and dissemination of cultural heritage, as can be seen in several key lines from the follow-up Treaty of Amsterdam (1997), Article 151 (ex. Article 128):

"2. Action by the Community shall be aimed at encouraging cooperation between Member States and, if necessary, supporting and supplementing their action in the following areas:
- improvement of the knowledge and dissemination of the culture and history of the European people;
- conservation and safeguarding of cultural heritage of European significance;
- non-commercial cultural exchanges; …" and

"3. The Community and the Member States shall foster cooperation with third countries and the competent international organisations in the sphere of culture, in particular the Council of Europe."

What concerns conservators and curators, is that this not only implies, but also has directly resulted in an increase in the number of loans and special exhibitions of objects. This increased movement of cultural heritage brings with it certain dangers, not only the well-known dangers of (irreparable) damage in transport or due to poor exhibition conditions, but increasing exposure of objects to the possibility of loss or theft as well.

The general public is aware of spectacular thefts such as the armed robbery of Edvard Munch's "The Scream" from the Munch Museum in Oslo, Norway, in October 2005, or the break-in at the Van Gogh Museum in Amsterdam in December 2002. In addition, thousands of lesser known but, from a cultural and historical standpoint, equally valuable objects are waiting to be found, listed, for example, on the Art Loss Register, the ICOM Red List, and/or Interpol's "Stolen Works of Art" CD-ROM [1, 2, 3]. However, this is just the tip of the iceberg of a much more serious problem, only now getting public attention due to the controversy surrounding the source of objects found, among others, in the J. Paul Getty collection or the Metropolitan Museum of Art, New York City. The illicit trafficking of stolen objects has been a problem for centuries, and continues to be a major problem to this day for archaeological sites and museums which lie unprotected in war zones such as in Afghanistan and Iraq. The greed of unscrupulous collectors and looters alike has resulted in the removal, damage, and/or loss of countless numbers of objects, both in the physical and economic sense, as well as in historical context.

2 The problem of the identification of objects

A key problem in fighting the illegal trafficking of objects is their irrefutable identification. Museum objects are generally identified using some sort of cataloguing system. The objects may be (digitally) photographed, and then marked using a sticker, perhaps with a barcode, or a marker. This information is then entered into a paper or modern software catalogue / database along with other descriptive and historic information, condition reports, etc. Besides the fact that stickers and markers have the disadvantage of reacting with the objects they are applied to, they have the additional disadvantage that they can be removed and/or forged.

In the field, in particular, in archaeological sites in third world countries, the identification of objects can be far more difficult. Due to time constraints and/or the sheer number of objects, if an object is documented at all, it is often with a rudimentary sketch and/or photograph, and perhaps a label. At a dig in progress, many objects will lie undiscovered and thus undocumented due to similar time constraints, and thus easy prey for thieves at an unsecured site. Further, it has been found, that larger objects such as stone slabs may be broken apart for easier transport and sale by thieves [4].

In any case, when objects come through a customs checkpoint, much depends on the customs officer's knowledge and expertise to recognise an object for what it is, whether stolen or not. Given the number and wide variety of objects in circulation, this is a virtually impossible task. There is thus a need for a method for identifying objects quickly and uniquely, without doubt.

3 Fingerprinting objects: the European project FING-ART-PRINT

A European project, FING-ART-PRINT has recently been started with the objective of providing this method for uniquely identifying objects. The FING-ART-PRINT technique involves taking a unique "fingerprint" of an object. This fingerprint consists of the measurement of the roughness and reflectance spectra (colour) of an object at some position on the object, for example, a square centimetre, selected by the owner. A prototype apparatus for taking the fingerprint will be developed and optimised with the help of end users from museums and other cultural heritage institutes. A protocol for taking the fingerprint will also be developed, as well as an initial draft of standards for their use.

3.1 The fingerprint of an object

An example of the information contained in such a fingerprint is shown in Fig. 1. Here, the roughness has been measured of a 3.5 × 3.5 mm area marked in the painting, Fig. 1ab. The roughness measurement itself is shown in Fig. 1c [from 5]. This is a false colour image of the area, where the colours indicate height, red being high, and blue being low. The roughness was measured using a non-contact method, white light confocal profilometry. Such a profilometer works based on the simple principle of focussing a standard light microscope. In order to focus on an object using a light microscope, the user rotates the focussing knob on the microscope,

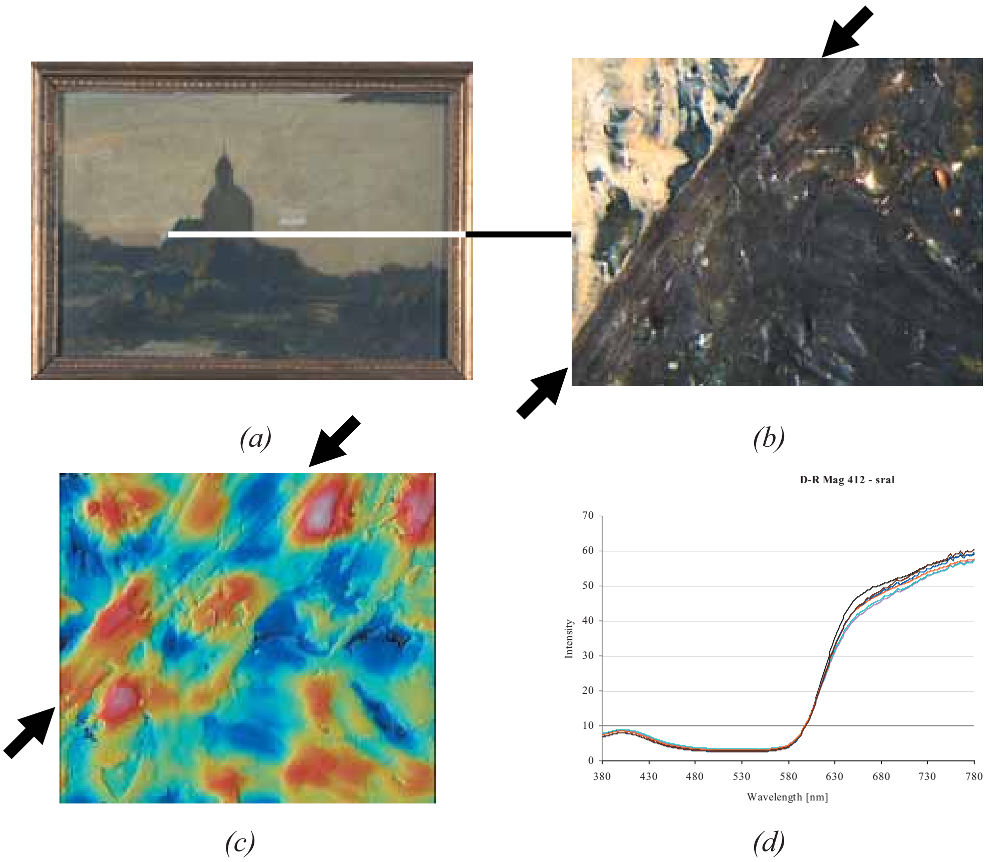

Figure 1: Example of the fingerprint of a painting (arrows in b and c show same brushstroke): a) "Dorpskerk bij Avond (Village Church in the Evening)" by I.J. Wennin, b) 3.5 mm × 3.5 mm area used for roughness measurement, c) Roughness measurement (red is high, blue is low), d) Example of reflectance spectrum

which moves the objective lens up and down until the specimen is in focus. By scanning across the surface of an object, the profilometer follows the height / topography of the surface by automatically keeping it in focus. The movement of the objective lens is then a direct measurement of the height of the object as it moves along the surface. By using confocal techniques, height resolutions down to nanometer scale can be obtained [6, 7].

In Fig. 1c, the round red areas correspond to the regular high points found in the weave of the canvas. The diagonal stripes in the image are of particular interest however. These are the actual brush strokes used by the artist, as can be seen by comparing Fig. 1c with the colour digital image in Fig. 1b, see arrows. It should be noted that both the height and spatial resolution of Fig. 1b are 4 micrometers. Spatial resolutions down to 1 micrometer are possible, and are at the level of individual pigment particles. Assuming that someone even knew where the fingerprint was taken, such a fingerprint would thus be impossible to forge by hand, also taking into consideration that it must continuously "flow" into the neighbouring regions of the painted area. It is, in fact, unique, being the painter's "signature".

An example of a reflectance spectrum in the visible light range is shown in Fig. 1d. Such a diagram gives the intensity of each wavelength of visible light reflected from the surface, the combination of which is responsible for the colour of the object. Such spectra are also unique for a particular paint [8, 9], and can thus also be considered a fingerprint of the (painted) object. A prototype imaging spectral interferometer will be optimised into a commercially viable instrument for FING-ART-PRINT. This instrument will also be able to provide reflectance (colour) information at micrometer spatial resolutions similar to that of the profilometer. Combined with the roughness measurement, the object provides, via FING-ART-PRINT, its own unique identification marking.

3.2 Fingerprinting equipment and methodology

The equipment for taking fingerprints of objects will consist of a (trans)portable combination of a confocal white light profilometer and an imaging spectral interferometer. The confocal white light profilometer is a modern, commercially available instrument designed and manufactured by FING-ART-PRINT partner NanoFocus AG, Oberhausen, Germany. The imaging spectral interferometer is under development by FING-ART-PRINT partner ELDIM S.A., Herouville St. Clair (Caen), France, with the assistance of the University Pierre et Marie Curie. Both instruments will be mounted on a stable, robot arm, capable of manoeuvring the instruments to almost any area selected by the owner on a two- or three-dimensional object. The robot arm will have to be virtually vibration-free to enable the user to obtain the high resolutions required for the roughness measurements.

User-friendly software will be written by the University of Southampton with the aim of allowing non-technical museum personnel to obtain fingerprints “at the touch of a button”. They can be assisted by technical staff who will have access to a background software interface. The fingerprint itself can have the form, for example, of a standard .tif or .jpg file which is easily read into any database. Further features of the software included semi-automatic relocation and matching of fingerprints.

Besides equipment development, a methodology and procedures for taking fingerprints will be developed during the project, taking user requirements into account. Initial considerations are being made on the issue of the safety of the object, and cleaning / restoration. For the safety of the object, the fingerprint should preferably be taken with the equipment placed to the side of the object, as opposed to above it. For example, fingerprints of paintings should be taken with the painting hanging in place in exhibition, and fingerprints of ceramic figurines should be taken of positions on the side of the object, or on surfaces facing slightly downwards. Further, the sensor head should not come closer than 10 mm (profilometer lens) to the object, and starting and stopping the motion of the sensor head will be manually performed.

In general, objects should be cleaned and restored before a fingerprint is taken. However, in the case of cleaning, this is not always the obvious choice. In many cases, ethical considerations of whether soil, residues, etc. are part of the historical value of an object may preclude cleaning. This may then become a problem for the durability of the fingerprint, especially in the case of loose layers, see section 4.2.

4 Applications and limits of the FING-ART-PRINT system

4.1 Applications

As a *non-contact* method for uniquely “marking” and identifying objects, FING-ART-PRINT will have a number of important applications. Since an object essentially marks and identifies itself, there is no more need for stickers or marking pens. The standard .tif/.jpeg fingerprint can thus be used in museum and collection databases for archiving and documentation purposes, and for “marking” objects after restoration work. As such, it can also be used within tracking and tracing systems for the transport of objects. The fingerprint can be sent along with an object, for example, stored on a CD, or as part of a GPS enabled tracker or smartcard chip. It can be checked upon arrival at the object’s destination, whether at a special visiting exhibition, or upon return to the owner. In the case of the loss and recovery of an object, a fingerprint of the object can be taken and compared with a database of object fingerprints, in exactly the same manner as law enforcement officers use fingerprints, DNA, or dental records to identify missing persons, criminals, or potential personnel security problems. Note that the FING-ART-PRINT method is for identifying a particular object. FING-ART-PRINT, as well as other image recognition systems, cannot be used on its own to authenticate objects.

FING-ART-PRINT can also play a significant role in reducing the illegal trafficking of cultural heritage. A (trans)portable instrument would allow for much more rapid “marking” and documentation of objects at archaeological sites. If an international standard required that all objects were sold with a fingerprint, as well as with the proper papers and certificates of ownership and authenticity, raiding such a site would become far less interesting, since it would become extremely difficult for thieves to sell objects on the open market. Also conceivable is the use of permanently placed readers at customs checkpoints, analogous to barcode checkout counters at the supermarket [10]. If, in addition to owner-selected fingerprints, there were a standard requiring the fingerprinting of objects at a specific position (vertical and/or horizontal position), customs officers could fingerprint objects and compare them with international databases of objects, stolen, or in legal hands. This would greatly assist them, as many custom officials do not have the expertise to recognise authentic objects, let alone, objects that have been stolen.

4.2 Durability of the FING-ART-PRINT

A further technical objective of the FING-ART-PRINT project is to determine the durability of the fingerprint. Whereas a human fingerprint remains with its owner throughout his/her entire life, the fingerprint of an object may change with time. The objective of FING-ART-PRINT is to only have to fingerprint an object once in a “long” period of time. This must be a “reasonable” amount of time, depending on the application for example, the time between conservation treatments of an object which is generally measured in tens of years.

A number of factors which can possibly lead to a change in the fingerprint of an object will be investigated during the FING-ART-PRINT. These include:

- Aging and discolouration leading to well known yellowing of varnishes or discolouration of paints. This can occur under the influence of climate (temperature and relative humidity), light, and/or atmospheric pollutants. Chemical reactions can also lead to a change in the surface roughness.
- The surface geometry of a varnish or paint layer could also change over time. This would be particularly true for contemporary or revarnished works, where long-term drying and aging effects are still strong.
- Damage due to wear, poor handling, or aging: Accidental (or intentional) damage to the fingerprint can lead to partial or total obliteration of a fingerprint. Protocols must be developed to deal with partial fingerprints as is done in normal criminal justice work.
- Cleaning of an object, and in particular, the removal of dirt and deposits will definitely affect the fingerprint. Fingerprinting protocols must account for this, and in fact, it is already recommended that the fingerprint should taken after cleaning and restoration treatment, if (ethically) possible. This would be, however, more difficult in the field.

5 Case studies

In order to test the various issues surrounding FING-ART-PRINT, a series of case studies are being conducted with real museum objects. Just prior to the presentation of this paper, 29 objects were fingerprinted using the roughness measurements only at NanoFocus AG. These objects were submitted by the following eight Dutch museums, two non-museum collections (of which one was Greek), one commercial Dutch art gallery, and one police department:

- Allard Pierson Museum (Amsterdam)

- Amsterdam Historic Museum (Amsterdam)
- Amsterdam Police Department
- Army (Leger) Museum (Delft) via the Museum Security Network (Rotterdam)
- Frans Hals Museum (Haarlem)
- Galerij Fons Welters (Amsterdam)
- Kröller-Müller Museum (Otterlo)
- Museum Boijmans van Beuningen (Rotterdam)
- National Museum for Ethnography (Leiden)
- Netherlands Institute for Cultural Heritage (Rijswijk and Amsterdam; FING-ART-PRINT partner)
- Ormylia Art Diagnostic Centre of the Sacred Convent of the Annunciation (Ormylia, Greece; FING-ART-PRINT partner)
- Van Gogh Museum (Amsterdam)

A wide variety of objects were provided including paintings, metal sculpture of which two objects came from the same mould, ceramic sculpture and porcelain, archaeological objects, two copies of the same book, and two prints of the same lithograph.

The case studies are being conducted in order to
- develop the fingerprinting method, and identify and solve logistical and measurement problems
- find solutions for relocating fingerprints
- find solutions for fingerprinting objects with complex shapes
- see if unique fingerprints can be obtained from different objects cast from the same mould, or copies of works printed from the same press
- determine the effect of aging on the durability of fingerprints.

The measurements will be repeated next year at a planned FING-ART-PRINT workshop, and then again at a second workshop to be held shortly before the end of the programme. These future measurements will then include spectral reflectance measurements as well.

6 Conclusion

A new non-contact method is being developed for the identification, tracing, and protection of objects of art and cultural heritage against theft and illegal trafficking. Developed within an ongoing European project, FING-ART-PRINT, this method involves taking a “fingerprint” of an object consisting of a roughness and spectral reflectance (colour) measurements on a micrometer scale.

This fingerprinting technology is expected to have an enormous impact on the identification and protection of moveable cultural heritage (FP6 – Policy oriented research Priority 8.1.3.6). It makes innovative use of advanced technologies developed for “normal” industrial use in order to provide fingerprint records of objects of art and cultural heritage, this without any physical contact with the object, and non-destructively. The uniqueness of the fingerprints will allow the development of an international database for such objects, beginning with those more likely to be on display and/or loan. This is a particularly important development on a European level, given its open internal borders, the ease of transport between countries, and the desire for objects on loan, and/or complete travelling exhibitions. The development of such a database has not been possible up to now because of the lack of a reliable and standard non-contact method for identifying and documenting such objects.

It should also be noted, that the use of the properties of a (painted) surface as a “fingerprint” of an object has, to the wide knowledge of the FING-ART-PRINT partnership, never been considered in the literature. Although a number of research groups have used advanced technologies, mostly based on laser scanning, for documenting objects, the use of surface (paint) properties has never been considered for use as a fingerprint. This is partly due to the lack of resolution of those laser techniques, and partly due to the fact that previous goals were the documentation of objects and monuments for virtual museums, where high spatial resolution is not the main requirement.

7 European project details

FING-ART-PRINT, Contract No. 022453, Fingerprinting Art and Cultural Heritage – *In Situ* 3D Non-Contact Microscale Documentation and Identification of Paintings and Polychrome Objects, Coordinator: Dr. W. Wei, Netherlands Institute for Cultural Heritage, Amsterdam, The Netherlands.

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Development of a new antigraffiti system, based on traditional concepts, preventing damage of architectural heritage materials

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Key words: restoration, antigraffiti coatings, porous materials, monuments, surface treatments

1 The problem of graffiti

Graffiti is a major, increasing danger to Cultural Heritage, as in the last years there has been a high increase of this type of dubious works of art, mostly in urban areas. Apart from aesthetics aspects, interactions of graffiti with substrate, as well as cleaning procedures, threaten historical substance. The problem is especially severe for monuments made of porous materials, such as natural stone, bricks and lime mortars. These are especially liable to absorb the graffiti colorants; therefore they are extremely difficult to remove. In addition to this, the all established removal procedures deteriorate the surface to be cleaned gradually, so that repeated actions are not tolerable. In consequence, damage to historical monuments is most severe. Two major kind of coatings are currently being used for protecting surfaces against graffiti [1]: permanent and sacrificial. The first type (permanent system) is applied as a coating with low surface energy, which hinders the colorant formulation from entering the substrate that weakens the adhesion of the graffiti on the surface, so it can be removed by relatively mild procedures and solvent products [2]. Typically, polyurethanes or fluorocarbon modified paints are used for this purpose [3, 4, 5]. Whereas for materials of low porosity, such as metals and concrete, this strategy gives acceptable results, it is hard to apply it to materials of high porosity, because the natural transport of humidity through the substrate is critically hindered. Moreover, the adhesion usually is insufficient, especially in highly salted ancient building materials [6]. Lately, this treatment is irreversible, i.e., such coatings are permanent, what is not acceptable for treatment of historical monuments. The second system (sacrificial system), mainly based on acrylic, waxed and silicones, [7] makes appeal to sacrificial protective coatings that can be easily removed (or that do so spontaneously upon ageing). In this case, the colorant formulation is blocked from entering the substrate. However, the adhesion of the graffiti on the surface is strong, so that it cannot be removed as such, but the protective coating must be removed with the graffiti. This procedure is expensive, and the removal procedures using high-pressure-water-systems do still damage the underground. Frequent protection / cleaning treatments, therefore, result in a gradual destruction of the monuments' surface. Furthermore, in many cases problems have been encountered with a very limited durability of the protection itself: alteration by the sun, rain, etc. that may cause a fast disappearance of the protection. Since this disappearance is not always clearly visible, graffiti may cause remaining damage to walls, which were thought to be protected by an antigraffiti system. Polymer hybrid systems, with polysiloxane and fluoropolymers, where a sacrificial top coating covers a permanent primer coating [8], have been employed frequently in past years for this purpose [9, 10, 11]. For historical monuments, this system suffers from the same problems as the simple permanent coatings, and thus it is not appropriate, either. In short, the present permanent, sacrificial and hybrid antigraffiti systems do not fit the requirements needed to protect Cultural Heritage, thus usually causing an irreversible damage to the monument, which obliges to limit as much as possible the use of these products. In view of this situation, there is a strong need of developing a new protection system especially designed for these ancient porous construction materials.

2 A new antigraffiti system specifically designed for architectural heritage materials

The main objective of the GRAFFITAGE project is to develop novel conservation coatings suited for protecting materials of historical monuments, based on a similar structure of ancient protein coatings, avoiding the disadvantages of currently used antigraffiti coatings. This system ensures the advantages of the present used antigraffiti coatings (permanent and sacrificial), and is characterised as:

- Having low surface energy
- Permanent under out-door conditions, with durability against environmental agents similar to traditional polyurethane or fluorinated systems
- 100% reversible to especially designed mild cleaning systems or especial environment not attacking agents
- Permeable to water vapour, getting values for water vapour reduction similar to sacrificial systems
- Impermeable to liquid water, with similar values to commercial waterproofing products
- Transparent and low gloss, getting invisible to visual inspection.

2.1 Description of the product

A completely innovative approach will be used to develop the new antigraffiti system. This will be based on the complexation of polyampholytes with polymeric amines that are modified by fluorocarbon residues, specifically suited for the protection of currently used antigraffiti coatings. These polyampholytes are “protein-mimics” having a structural similarity with traditional coatings, like casein, gelatine and egg-white. These products will be a new generation of antigraffiti coatings, specifically suited for the protection of monuments, which after further development, could be commercialised and applied by SMEs involved in this market.

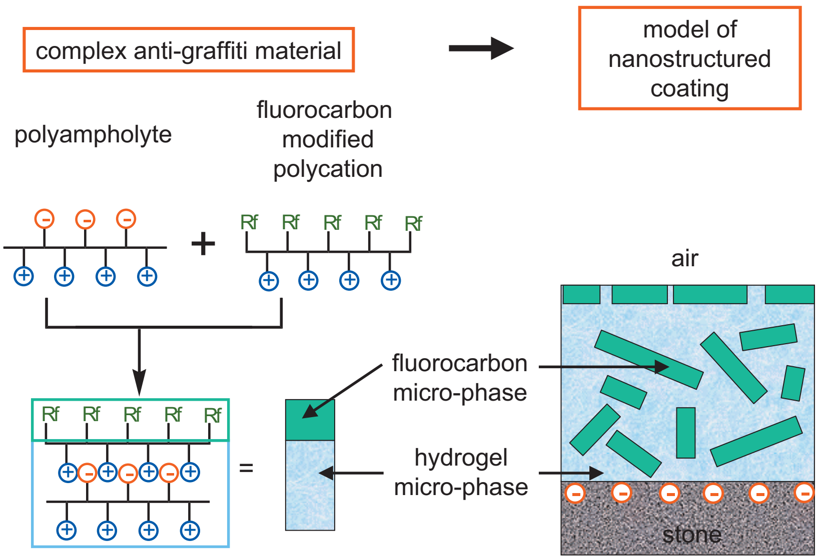

Figure 1: Description of the structure of the new antigraffiti system

3 Conclusions

3.1 European Dimension

The problem of graffiti aggression to monuments has European dimension, as it is typically found in most European large cities. More than 3.500.000 protected monuments have already been affected by this phenomenon [12]. Besides, the antigraffiti market has, nowadays, European dimension, gained through the manufacturing of products in some countries, and the distribution of existing products all over Europe. Therefore, the applicability of developed products should take into account the different materials existing within the E.U. and Associated Countries, as well as the different climates and environmental conditions within Europe, in order to ensure the overall reliable behaviour of these products. This situation obliges to undertake the project at European level, instead of at regional level.

3.1.1 Contribution to standards

Nowadays there are not standards of widespread use that serve for qualifying the performance of antigraffiti system: there are not any European Standards directly related to the assessment of antigraffiti performance in different substrates, such as stone, brick or mortars. Mostly based on the adaptation of EN Standards, RILEM and NORMAL recommendations, new procedures will be developed for testing different substrates and coatings, to the specific case of antigraffiti applied on ancient materials. The development of these procedures and limit values is the previous work for a further EN Standard development.

3.2 Innovation and originality

The present permanent, sacrificial and hybrid antigraffiti systems do not fit the requirements needed to protect Cultural Heritage, thus usually causing an irreversible damage to monument, which obliges to limit as much as possible the use of these products. Recent studies on the basic chemical behaviour on polyampholyte complexes and fluorocarbon residues [13, 14, 15] have led to the idea of their use as antigraffiti coatings mixing polyampholytes with polymeric amines, modified by fluorocarbon residues, which will be the approach of this project. Structures based on charged polymers and complementary fluorocarbon surfactants have been applied before as protecting coatings, including antigraffiti [11]. However, their use was unsatisfactory for antigraffiti due to their low mechanical stability and poor ageing behaviour. This project implies the making of a totally new formulation of one chemical product with the aim of providing an antigraffiti system compatible with porous substrates of historic buildings. Such formulation is based on the replacement of the low molar mass surfactants by high molar mass amphiphiles shall strongly improve the performance. Furthermore, the replacement of the hitherto used polyelectrolytes by a polyampholyte, and the choice of protonated polyamines instead of quaternized polyammonium salts will allow the facile removal of the coating under basic conditions.

3.3 Impacts

3.3.1 Industrial impact

The GRAFFITAGE project has an important industrial impact, having a strong influence in the market share of a variety of industrial sectors like antigraffiti manufacturers and suppliers, restorers and graffiti cleaners, architects and decision makers of monuments restoration, owners of monuments, etc. Antigraffiti are a typical business for SMEs: small market, individual solutions are required case by case, experienced work force and much know-how required for practical implementation. The development of antigraffiti for Cultural Heritage is so far delayed by conflicting requirements (efficient protection with minimal modification of historical substance) and by high financial risk (high development costs, no free market for exploiting new products). At the moment, this market is covered mainly by European SMEs, as well as some European and American large companies (the ratio American / European antigraffiti producers selling their products in Europe is 2). The development of the project will highly benefit the competitiveness of European SMEs with respect to large American antigraffiti producers. Two types of antigraffiti systems are used nowadays to protect monuments. The permanent system does not suit the requirements of Cultural Heritage materials. As a consequence of this, its use in this field is coming down and is being forbidden in some countries. The sacrificial systems are very expensive, not only because of the product cost, but also because of the high cleaning and replacement cost of the coating every time the graffiti is removed. The effectiveness of antigraffiti is not a matter of efficient prophylaxis, but mainly it is a matter of keeping surfaces cleaned. If a place is continuously kept cleaned, sprayers and graffiti-makers will be less tempted to paint. The main problem is that owners of monuments and other related bodies are not able to maintain the places cleaned continuously, mostly because the small government money and the existence of other higher priorities, such as reconstruction and maintenance. For this reason, the most important in this field is finding an effective protective coating (which suits the basic demands in Cultural Heritage) which is easy to clean with a low cost maintenance. In this sense, the GRAFFITAGE project is aimed at developing a new permanent reversible coating able to eliminate graffiti produced on it in an easy and inexpensive way. Therefore, the commercialisation and further application of the project will considerably reduce cleaning and maintenance costs of treated surfaces. In consequence, considering the suitability of the product for Cultural Heritage, and the reduction of maintenance costs, the application of antigraffiti in monuments is expected to increase dramatically. The impact of the development of this project is not only addressed to economical direct aspects, but also it has an important influence on the conservation degree of our monuments, that strongly influences the economy of a region or city.

3.3.2 Societal impact

The societal impact of all work carried out to preserve European Cultural Heritage is enormous. The GRAFFITAGE project will contribute to benefit European society by promoting the adequate conservation of monuments and other Cultural Heritage. The visual effect that graffiti aggressions cause in monuments and the social meaning of these expressive actions (mostly related to social protests and vandalism) produces stronger societal impact than other types of monument decay. Therefore, the maintenance of monuments against these aggressions has a very connotative societal effect. The design of a new antigraffiti product able to eliminate graffiti produced in an easy and inexpensive way would considerably reduce cleaning and maintenance costs of treated surfaces. In consequence, the application of antigraffiti in monuments is expected to increase dramatically.

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Session II

Innovative applications and new ideas: immovable heritage

Mapping climate change and cultural heritage

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Key words: climate change, environment, building cultural heritage, landscape

1 Introduction

Climate change is currently attracting interest both at research and policy levels, but the focus tends to be on issues such as agriculture, lakes and forests. Cultural heritage, in particular built heritage, archaeological sites and cultural landscapes, has not yet been dealt with in programmes or publications either at the EU or global level [1].

Up to now, climate change has never been taken into consideration as a factor threatening cultural heritage [2], which is a non-renewable resource to be transmitted to future generations [3, 4].

The Noah' Ark Project funded by European Commission demonstrates a novel synergy between climate change and cultural heritage research. This project aims to fill the gap existing in studies on the effects of future climate variations on cultural heritage, confronting for the first time the problems arising from the impact of climate changes on Europe's built heritage and cultural landscape [5].

Initial work has identified the most significant climate parameters affecting cultural heritage. Outputs from Hadley Models (HADCM3 and HADRM3) have been used to provide a picture of the European climate from 1961 to 2099.

These data are employed to produce hierarchical maps aiming to present broad regional future threats to European monuments and buildings over the next 100 years, i.e. climate maps, heritage climate maps, damage maps, risks maps and thematic maps.

2 Climate models

Climate parameters used for future projections are extracted by the models of the Hadley Centre (U.K.): HadCM3 and HadRM3.

HadCM3 is an Atmosphere-Ocean General Circulation Model. Its grid resolution is 2.5×3.75 degrees (i.e. 295×278 km at 45 N latitude).

HadRM3 is a Regional Climate Model. It encompasses a European region at a much higher resolution than the HadCM3 model. The temporal span is from 2070 to 2099 and it is based on a grid of equal-area cells, 50×50 km (i.e. 0.5×0.5 degree at 45 N latitude).

The model output used for our analysis has relied on A2 scenarios, which are based on a very heterogeneous world, in which the underlying theme is that of strengthening regional cultural identities, with an emphasis on family values and local traditions, high population growth, and less concern for rapid economic development.
The selected geographical area is centred on Europe and covers a region of 33.75W – 67.50E latitude and 80N – 25N longitude for the general model, and 30W – 55E latitude and 72N – 35N longitude for the regional one.

The daily outputs of HadCM3 and HadRM3 have been used to elaborate variables critical to the built cultural heritage. The monthly, seasonal and yearly means of the following parameters have been produced:

Temperature derived parameters
Temperature range: $\max(T_1..T_n) - \min(T_1..T_n)$ where T_i = daily mean
Thermal shock: number of events when $Tmax(i)-Tmin(i) > X$ °C
where X = 7, 10, 15, 20 °C
Freeze-thaw cycles: number of cycles, a cycle occurs when
$T(i) > 1 \wedge T(m) < -3 \wedge T(n) > 1$
where T(i), T(n) and T(m) are daily means and $i < m < n$

Water derived parameters
Precipitation Amount
Rain days: total number of rainy days
Extreme rain: number of events when $P(i) > 20$ mm, where P(i) is the daily precipitation amount
Consecutive number of rainy days: number of events
Mean Relative Humidity
Relative Humidity range
Relative Humidity shocks

Wind derived parameters
Wind speed: mean $(W_1..W_n)$ where W is the daily mean
Wind speed counts: number of events when Wmax > Xm/s
where X = 7.5, 10, 15, 20 Wmax is the daily maximum

3 How can climate change be mapped for cultural heritage?

Using the HadCM3 data output, 30-year mean maps have been produced relative to 1961-1990 (Recent Past), 2010-2039 (Near Future) and 2070-2099 (Far Future), to provide three different pictures of several of the above mentioned parameters during the 1961-2099 period in the European area. The project has also generated difference maps between the 2010-2039 map and 1961-1990 map and between 2070-2099 map and 1961-1990 map, in order to quantify the changes that will occur in future respect to 1961-1990 (taken as reference). In addition, the 30-year mean maps relative to 2070-2099 have been produced using the HadRM3.

These data are utilized to produce hierarchical maps aimed at presenting broad regional future threats (Figure 1).

At the simplest level climate change has been mapped in terms of traditional climate parameters relevant to cultural heritage (e.g. yearly precipitation, rainfall intensity, frost).They represent the basis for the other types of maps and are functional to their preparation (Figure 2).

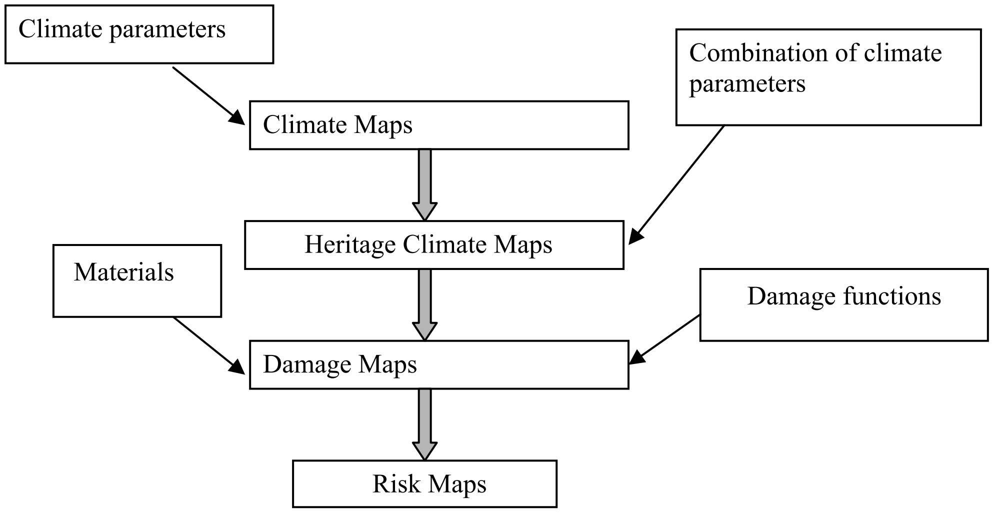

Figure 1: Scheme of the hierarchical maps produced for illustrating climate change future threats to the built heritage

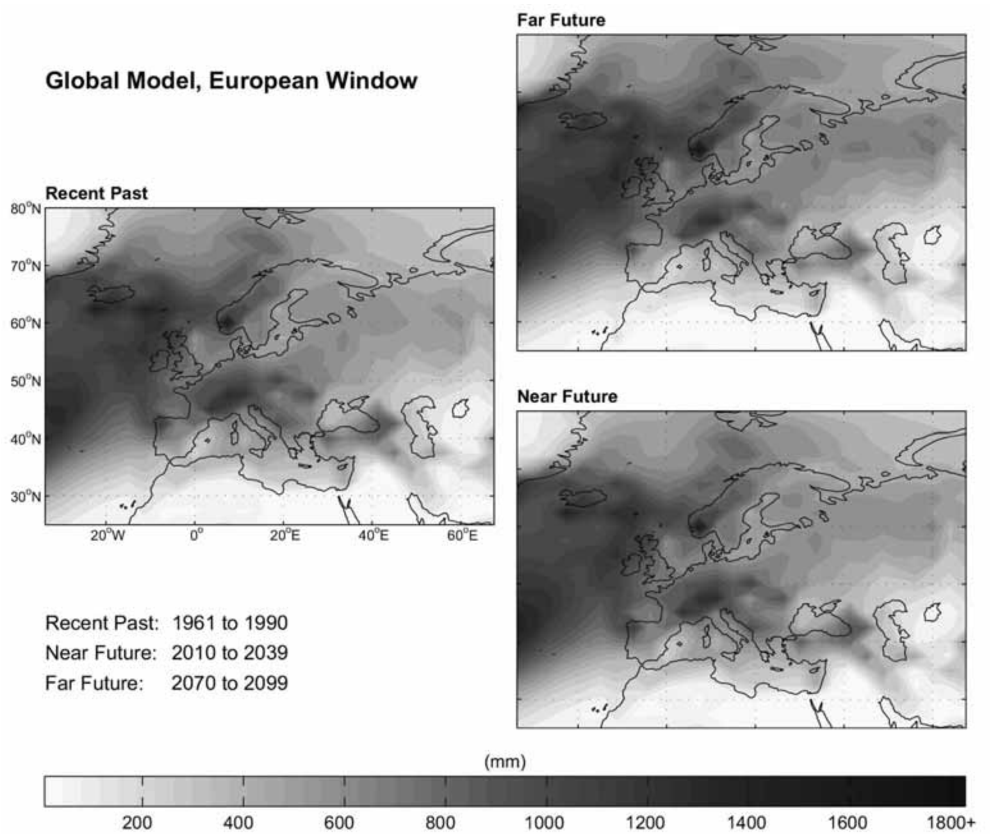

Figure 2: Yearly precipitation projections in Europe for the different periods analysed: recent past, mid future and far future – HADCM3 model

Furthermore climate parameters have been combined to produce specific heritage climatologies, e.g. wet-frost, based on rain followed by intense freezing.

A further step has made use of climate parameters to determine the amount of damage occurring on building materials in future scenarios. The damage maps are based on damage functions, which quantitatively express the damage induced by climate parameters on building materials (e.g. dissolution induced by rain, crack propagation during freezing, salt weathering of porous stones).

Finally risk maps are based on the combination of two or more damage processes that can occur in different regions of Europe. This decay evaluation can then be translated into generalized risk maps that can inform decision makers of the type of risk most prevalent in a particular region.

Mapping provides a strategic tool for a sustainable management of the future threat to cultural heritage and opens up a challenging new area for interdisciplinary research.

4 Conclusion

4.1 European dimension

Few interests of European citizens are of such great importance as the problems associated with global warming or climate change. Climate change can occur over areas of varying extension, outdoor as well as indoor. In terms of practical consequences, global, regional and local climate changes need to be distinguished. There is an urgent need to develop and apply policies, strategies and measures to mitigate the impact of global climate change on cultural heritage at all the three levels. All European states and local administrations, as well as stake holders, need tools for impact mitigation on the relevant level, i.e. global or continental, regional or municipal, and at site or object level. This approach is also justified by the fact that global change effects are frequently intensified due to climate change effects generated at lower levels.

Finally, the increased stresses and shorter maintenance periods will generate an increased cost linked to climate changes, in the form of financial support for the restoration and conservation of the built cultural heritage. The project methodology and results predicting future scenarios regarding the protection of cultural heritage will be also useful to the construction sector: building managers in general will need to understand the probable impacts of climate change on their building stock.

4.2 Innovation and originality

The results achieved within the Noah's Ark Project will lead to:

- the determination of the meteorological parameters and changes most critical to the built cultural heritage;
- research aimed at predicting and describing the effects of climate change on Europe's built cultural heritage over the next 100 years;
- the constitution of a scientific basis for the development of mitigation and adaptation strategies for historic buildings, sites, monuments and materials that are likely to be worst affected by climate change effects and associated disasters;
- the development of electronic information sources and tools, including Climate Risk Maps and a Vulnerability Atlas, aiding heritage managers to assess the threats of climate change, in order to visualize the built heritage and cultural landscape under future climate scenarios and model the effects of different adaptation strategies;
- advice for policy-makers and legislators.

4.3 Impacts

The Noah's Ark project has contributed to closing the gaps existing in current EU policy on air quality and impact assessment, with particular reference to "Ambient and air quality assessment and management (Council Directive/EC), the EC CAFE Directive (Clean Air For Europe) and the Environmental Impact Assessment (EIA Directive/EC), favouring the inclusion of Cultural Heritage.

In Climate Change Reports, such as the European Topic Centre Air and Climate Change (ETC-ACC) Report for the European Environment Agency (EEA), and in the Intergovernmental Panel on Climate Change Report (2001 and 3rd Assessment Report), cultural heritage is not mentioned among the expected future impacts and vulnerabilities. Within this context the EC funded Project Noah's Ark has a pioneering added value.

An additional impact of this research will be its usefulness to the European Insurance Industry. This value is recognised by the industry through the participation as a partner in the project of the Ecclesiastical Insurance Group, specialized in the insurance of historic buildings, particularly churches. Their data show an upward trend in the cost of environmental impacts on buildings, from annual claims worth approximately 750 million Euros in the early 1990's, to close to 1.5 billion Euros for their annual average over the recent three-year period from 1999-2001. The exceptional flooding in the UK during 2000 resulted in insured losses more than 2.2 billion Euros. An improved understanding of the likely effects of climate change will enable a better business management. The research to test and improve drying-out scenarios for flooded buildings will lead to a more efficient drying out of buildings, and in the long run, lower costs, as damage to the historic fabric caused by inappropriate drying out strategies will be avoided. The research will also enable the time required for the drying-out of individual buildings to be more accurately estimated and planned, leading to better management of this process and its costs.

5 Acknowledgement

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Norwegian Institute for Air Research (Norway)
Ecclesiastical Insurance Group (UK)
Biologia Medio Ambiente Ltd. (Spain)

6 European Project Details

NOAH's ARK, Contract SSPI-CT-2003-501837 'Global Climate Change Impact on Built Heritage and Cultural Landscapes'
Coordinator: Cristina Sabbioni, Institute of Atmospheric Sciences and Climate, National Research Council, Ital. Email address: c.sabbioni@isac.cnr.it

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Salt crystallization and damage on monument: the issue to isolate or to eliminate entrapped sea-salts

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Key words: sea-salts, cultural heritage, conservative treatments, decay patterns

Abstract
To safeguard buildings and monuments of territories where the behavior of stone and brick masonry is conditioned by marine environment two EC Projects have considered the problem to: a) prepare, apply and control suitable product for conservative interventions on surface able to prevent further penetration by sea-salts and to immobilize the already present salts creating a "memory effect" (Asset Project 2001-2004); b) to assess possibilities and limitation of desalinations treatments (Desalination Project 2006-2009).

The phases of research concerning the EC Asset Project have focused the methodology to quantify the damage of sea-salt on coastal zone, the selection of traditional and new generation treatments products, the consideration on possibilities and risks of treatments on salts loaded substrates. In the first phase it has been recognized and investigated the sea-salt sources (sea flooding, rising damp, marine aerosol), identified the decay patterns of coastal environment (sub-tidal zone, inter-tidal zone, supra-tidal zone) and defined moisture paths through the analyses of textural-structural material characteristics. The possibilities and risks of treatments on salt loaded substrates emerge from compared analysis of laboratory tests. Without specific information on substrate, the following limits and possible risks connected to the application of water repellent treatments in masonry contaminated with NaCl are expected: a) effectiveness (both penetration depth and water repellent effect) of treatments, solvent based as well as silane cream, is drastically reduced when they are applied on substrate with high NaCl load; b) salt crystallization damage can be enhanced by application of water repellent treatments on substrates already contaminated by NaCl: this happens not only in presence of rising damp in the wall, but may be already due to RH changes of air.

The Desalination Project uses the findings of the recently ended Asset Project taking the available results into account in an optimal way. Central scientific and technical objectives in the project are gaining a better understanding of salt transport mechanism between a salt laden substrate and a material applied on top of that and to assess possibilities and limitations of desalination treatments. Non-destructive techniques (NDT), nuclear magnetic resonance (NMR-scanner) will test-surfaces and different substrate-mortar / poultice combinations with different granulometry on which will be applied. Advanced techniques able to determine parameters and performance of the desalination systems will be used. One of the main results of Desalination Project will be a clear guideline on how to come to a choice of desalination systems. This is of much importance to the European decision makers and will be incorporated in a knowledge based decision tool. To help European SME's to improve their desalination systems, more scientific knowledge on the transport mechanism of desalination as well as practical methods to assess the quality of desalination are needed. The use of better desalination systems forms a clear step forward to a durable approach of maintenance in the cultural heritage. The second aim is to gain scientific knowledge on how desalination works.

1 Introduction

Salt decay processes, linked to marine aerosol, sea floods, rising damp and the saline content of the rainfall, are amongst the most recurrent and severe causes of damage to European cultural heritage. Due to climate changes, in the near future there will be an increased risk of floods in coastal areas and along the big European rivers. With the floods high amounts of salts can be introduced in walls of buildings, or already present salts will be activated, leading to a high risk of damage as soon as the structures begin to dry out. Since the buildings materials are systems lacking any form of regeneration mechanism, they tend to accumulate the salts they absorb and are unable to get rid of them. And what is even more serious is that aggressive substances accumulated because of exposure to pollution over a long period of time may well continue to be active even after the external environment could be restored to the pollution levels found in pre-industrial times.

The care of monuments threatened by sea-salt damaging mechanisms is a concern of European dimension: how to hinder or limit sea-salt damage to monumental buildings in the most efficient and durable way.

The development of methodologies to minimize sea-salt damage to historic buildings contributes to the reduction of the use of natural resources needed for retrofitting and for protection of historic buildings in the most effective way and consequently helps to reduce costs involved in the protection maintenance. The care of historic buildings is not only an esthetical duty but it is also necessary for the economy of a country considering tourism and cultural activities into or around monuments. Ineffective or inappropriate and even destructive conservation interventions are often applied to the various building materials under different microclimatic conditions without any knowledge of the specific sea-salt decay phenomena and mechanism triggered accordingly.

The EC Projects: ASSET (Assessment of suitable products for the conservative treatments of sea-salt decay) and DESALINATION (Assessment of mortar and poultices for historic masonry): research strategies and results.

Two EC Projects, ASSET (2001-2004) and DESALINATION (2006-2009), have considered respectively the issue: i) to immobilize the already present salts creating a “memory effect” and to prevent further penetration by sea-salts; ii) to assess possibilities and limitation of desalinations treatments.

1.1 ASSET Project

The approach to reach the objectives of the Project has started from the adjustment of a methodology to quantify the sea-salt damage, which considers three factors: sea-salt sources, building materials and decay patterns in coastal zone. The selection of traditional and new generation treatments products has supplied the performance of both water repellent and consolidant treatments on not contaminated substrates. The evaluations of the performance (possibilities and risks) of water repellent treatments on salt contaminated substrates were tested in the second phase of the research. The last phase of the Project has provided the criteria to define a standard methodology for the application of protective products.

An exhaustive overview of the damage provoked by sea-salt has been supplied by monuments and buildings selected in countries located along the European coastal belt (Fig. 1), every one of each is closely related to its environment, damage, materials, main sources of salts. The buildings selected as cases studies are located in Italy (Venice, brick and hard stone), The Netherlands (brick), France (La Rochelle, hard and soft stones) and Greece (Rhodes, soft stone), Fig. 2.

Figure 1: Marine aerosol, floods, rising damp and saline content of rainfall provoke an intensive stone decay of the historic, artistic and archaeological heritage of the European coastal belt

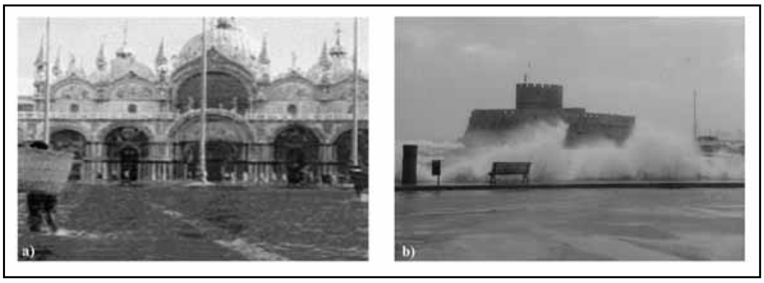

Figure 2: Sampling areas and sea-salt sources: sea flooding and rising damp in Venice and marine spray in Rhodes

The recognized and investigated sea-salt sources are: i) *sea flooding*, which occurs in subsidence areas due to withdrawal of underground waters, natural compaction of Quaternary sediments and sea level increasing; ii) *rising damp*, the phenomenon of capillarity, which rises from dispersed waters and superficial water tables, extending up the wall with persistent character; iii) *marine aerosol*, its source is the sea and its principal components correspond to those of sea water (Fig. 3).

As building materials hard stone and soft stone, characterized by granulometric variations and degree of cementation, as well as by structures of primary (bioturbations) and secondary (cracks), were considered. A great variety of decay forms have been observed in relation to susceptibility to the action of sea-salts depending on chemical composition and textural properties. Bricks, also different in chemical composition and textural properties, were analyzed (Fig. 4).

In order to ensure the singleness of the source of moisture and salts, analysis and measures have been performed in selected points: under 0.80 m on the medium sea level (sea flooded places); between + 0.50 and +3.00 m (places with prevalent rising damp); over + 7.00 m (places with only marine spray effect).

The decay patterns identified are related to the coastal environment with different characteristics that can be summarized as follows: a) sub-tidal zone; b) inter- tidal zone; c) supra-tidal zone (Fig. 5).

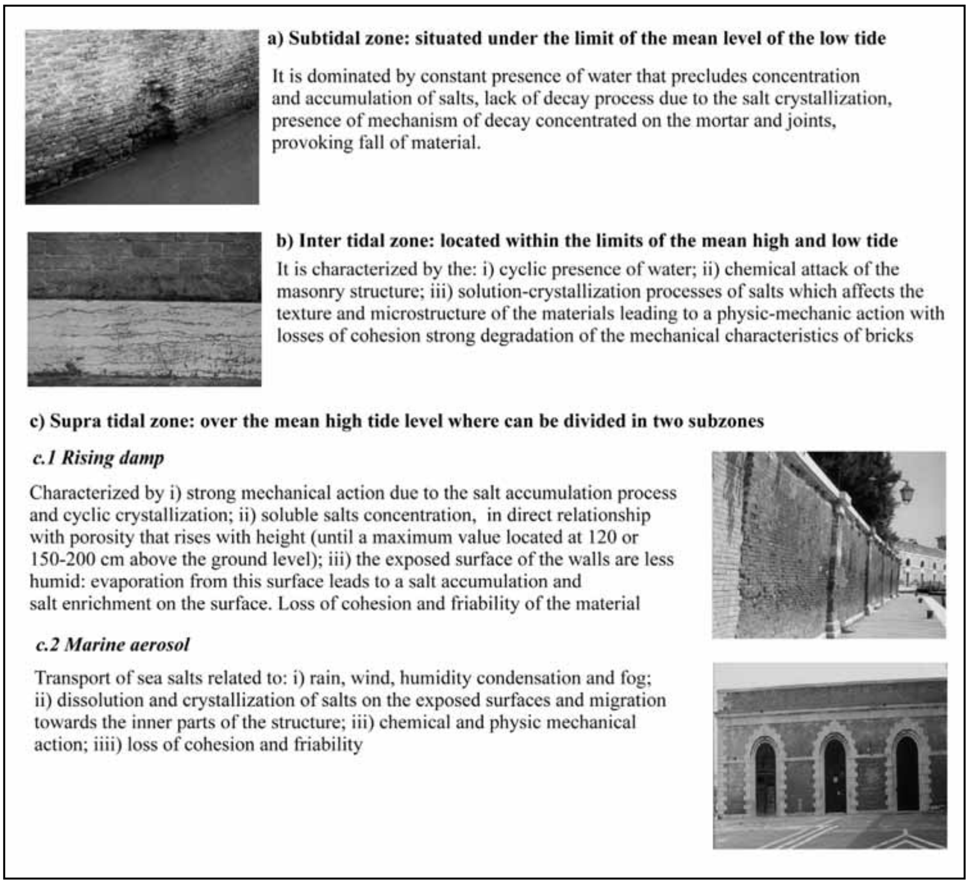

Figure 3: Sea-salt sources

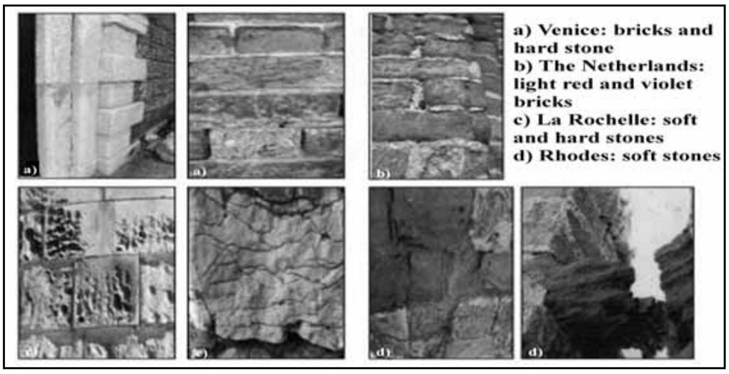

Figure 4: Building materials

The weathering, which affects the stones, is selective. Grains and/or calcitic cement, inorganic structures of primary and secondary origin (lamination, stylolites, recemented fractures), organic structures (fossils) and bioturbations influence the weathering forms. Also the textural and structural characteristics of bricks, depending on the moulding process, play an important role on the weathering. Different kinds of bricks were identified on the basis of micro-macroscopic analyses and of the properties that are able to take effect on water penetration process within bricks, influencing the ions concentration. Damaging processes due to the crystals expansion in the bricks create, as a consequence, crystallization pressures and destruction mechanisms according to grain composition and internal structures (wavy and convoluted lamination).

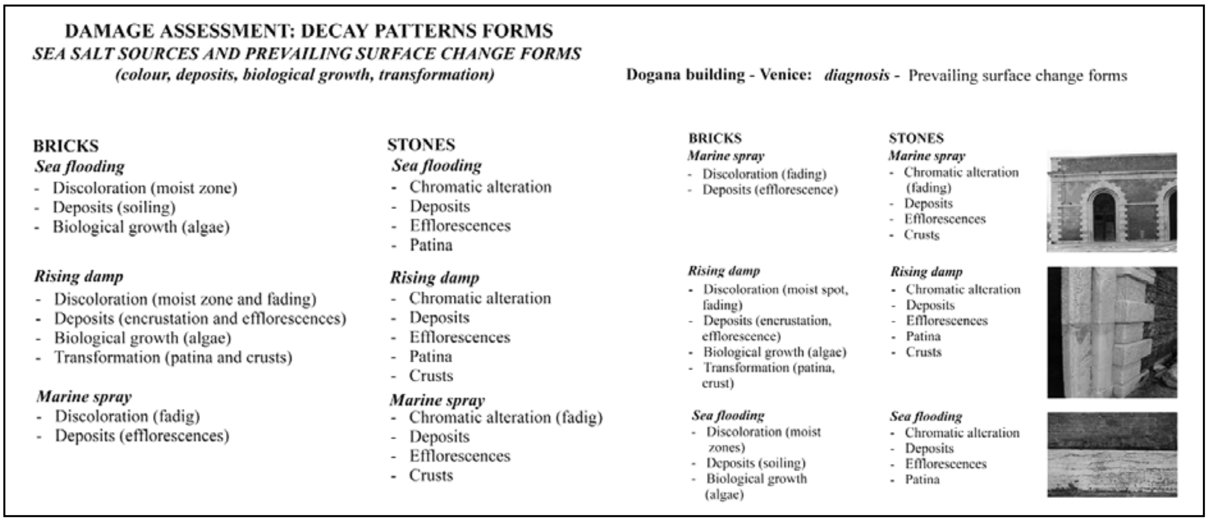

Figure 5: Decay patterns

According to deliverables of the Project (stone decay maps of stone damage levels) the elaboration of the following computerized maps related to sea-salt sources zones (sea flooding, rising damp and marine aerosol zones) was produced: i) structural and textural properties of building material (Fig. 6a); ii) moisture / sea-salt penetration into blocks / elements of the masonries according to structural properties of stones and bricks (Fig. 6b); iii) decay patterns of moisture / sea-salt penetration according to the masonry's morphology (Fig. 6c).

The second phase has evaluated, by means of laboratory tests and advanced analysis techniques, the performance of both traditional and recently developed products, applied on different types of stone, brick and masonry. The following parameters were investigated: i) products penetration depth in different materials, when applied before or after contamination with salt; ii) penetration quality and pores diameter reached by the products; iii) products effectiveness under circumstances of accelerated artificial ageing (wet-dry cycles, RH cycles, marine spray).

For the case studies, moisture and hygroscopic moisture profiles were determined for several wall sections in order to identify the origin of sea-salts and moisture. Additional analyses were performed to define: the salt type (X-ray diffraction, chemical analyses); the porosity (by immersion); the pore size distribution (Mercury Intrusion Porosimetry) and the chemical and petrographical (X-ray diffraction, chemical analyses, Polarising and Fluorescence Microscopy on thin sections) properties of the materials. The carried out investigation allowed to distinguish, in masonry, different zones according to the moisture and salt sources, to identify the damage mechanisms involved and to relate the material properties to the type and seriousness of damage.
Concerning the selection of the traditional and new generation treatment products, several liquid (traditional, both solvent based and water based) and cream water repellents were tested in the first phase of the research. The performance of both water repellent and consolidant treatments on not contaminated substrates were evaluated by means of laboratory tests in order to come a selection of products. The treatments were selected among the most diffused products used in the past years and the recently developed cream treatments. Information on the selected water repellent treatments is given in Tab. 1. On the basis of the results obtained the SBW and the CREAM S 0.04 g/cm^2 were selected as best performing products to be used in the second phase of the experimental research.

Table 1: Water repellent treatments tested in the first phase

Treatment code	General category	Components	Tested on
WG	Water glass (liquid)	potassium methyl siliconate and potassium hydroxide	Dutch brick, Venetian brick, Istria stone
SBW	Solvent based (liquid)	alkylalkoxysiloxane in aliphatic solvent	Dutch brick, Venetian brick, Istria stone
WBW	Water based (liquid)	Alkyalkolxysilane	Dutch brick, Venetian brick, Istria stone
CRM	silane/siloxane (cream)	silane/siloxane emulsion	Dutch brick, Venetian brick, Istria stone
CRM +	silane/siloxane (cream)	silane/siloxane emulsion with additives	Dutch brick, Venetian brick, Istria stone
CRM S	silane (cream)	Silane	Dutch brick, Venetian brick, Istria stone
RC80	Solvent based (liquid)	Ethyl-silicate + poly-methyl-siloxane mixture	Venetian brick
RC90	Solvent based (liquid)	Ethyl-silicate + poly-methyl-phenyl-siloxane mixture	Venetian brick
VP5035	Solvent based	Alkyl alkoxy silane	Venetian brick
BSM40SKI	Solvent based (anhydrous alcohol)	Monomolecular alkyl silane	Venetian brick

According to results obtained from a screening on the performance of traditional and new generation products, some water repellents and consolidants have been selected to be applied (i.e. case study Torre Alberaria in Venice), Tab. 2. After the removal of soluble salts from the substrate, some low-pressure water absorption measurements, by the Karsten-pipe method, were performed; cross sections collected from the building have been observed by scanning electron microscope (SEM) to evaluate the superficial morphology of applied products, their penetration in the pores of different size and their interaction with marine salts. X ray maps of selected elements were also collected to show the distribution and interaction of applied products and soluble salts. Investigations were performed by a SEM Philips Model XL 40 LaB6; X ray maps for different elements were obtained using an EDAX DX Prime X-ray Energy Dispersive Spectrometer, V = 25 keV.

Table 2: In situ tested products and their consumption

Commercial name	General category	Composition	Consumption (ml/m^2)
FUNCOSIL IC	water repellent (cream)	alkyl alkoxy silane and siloxane, emulsion in water	250
FUNCOSIL SNL	water repellent (liquid, solvent based)	alkylpolysiloxane, aliphatic hydrocarbons as solvent	775
Wacker VP5035	consolidant (liquid, solvent based)	alkyl alkoxy silane, organic solvent	787
RHOXIMAT HD RC80	water repellent (liquid, solvent based)	ethyl-silicate and poly-methyl-siloxane mixture, organic solvent	625
RHODORSIL RC90	consolidant (liquid, solvent based)	ethyl-silicate and poly-methyl-fenyl-siloxane mixture, organic solvent	600
DYNASYLAN BSM40SKI	water repellent (liquid, solvent based)	monomolecular alkyl alkoxy silane, anhydrous alchool as solvent	790

In order to consider the different sources of moisture and salts (sea-flooding, rising of groundwater and marine spray) that affect the building, a test area (about 25 m^2) was delimited (Fig. 7a).

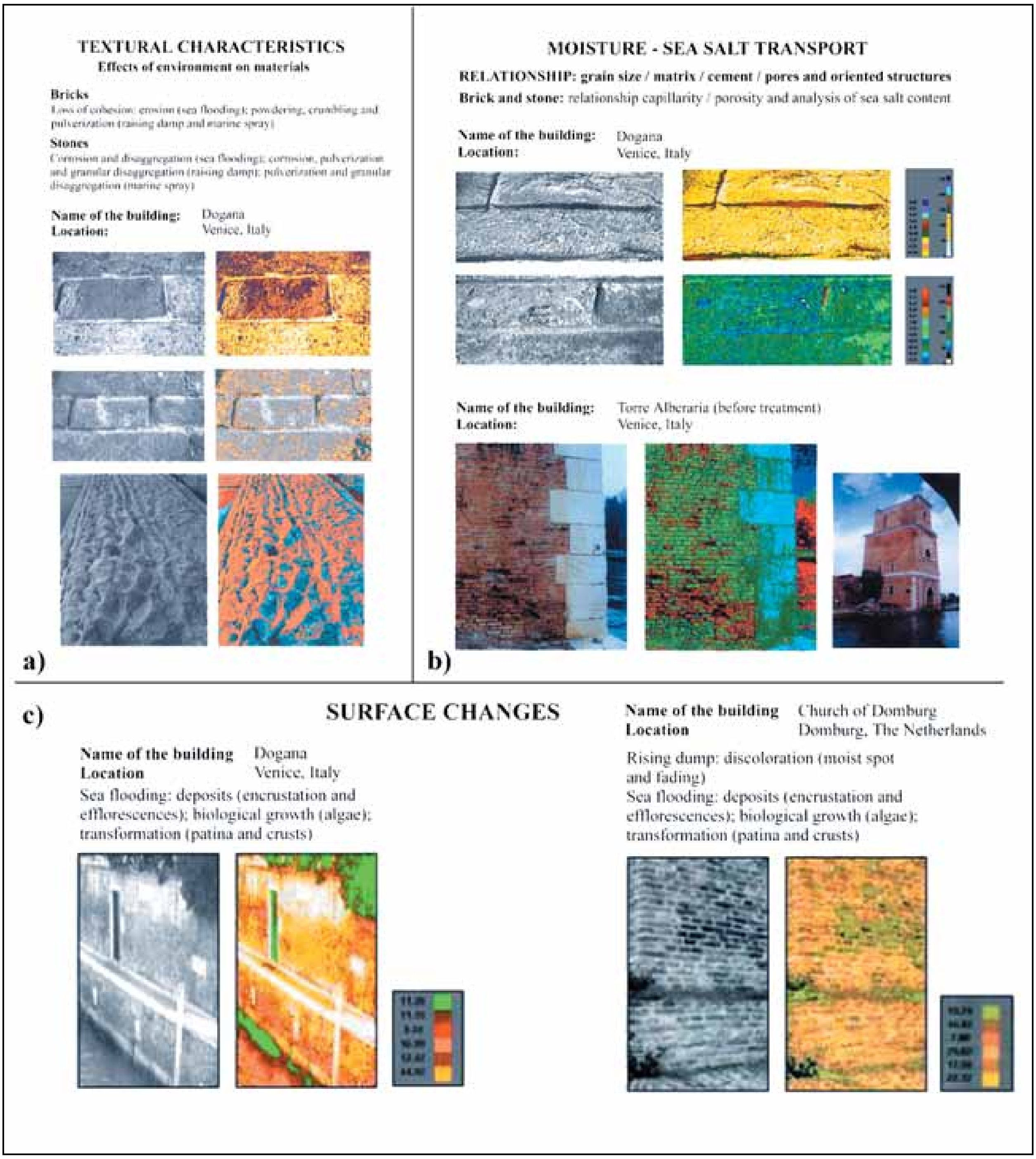

Figure 6: Damage assessment and decay patterns analysis by means of computerized non destructive analysis (ICAW technique) related to sea-salt sources zones (sea flooding, rising damp and marine aerosol zones): a) structural and textural properties of building material; b) moisture / sea-salt penetration into blocks / elements of the masonries according to structural properties of stones and bricks; c) decay patterns of moisture / sea-salt penetration according to the masonry's morphology

The laboratory tests have been supported by nuclear magnetic resonance (NMR), dynamic simulator and computerized analysis on treated and untreated samples. The nuclear magnetic resonance measures have been utilized to understand the moisture-salt transport in building materials and to follow the penetration of the applied products in the substrate assessing the final penetration depth (Fig. 7b). The experiments by dynamic simulator are fundamental for two aspects: to detect the importance of the porosity in the stone decay processes and to assess the treatment effectiveness on tested materials. The graphs "mass variation-time" give information related with material porosity and mass variations, due to first moisture absorption, and with quantity of lost material, due to mechanical action of the salt recrystallization (Fig. 7c).

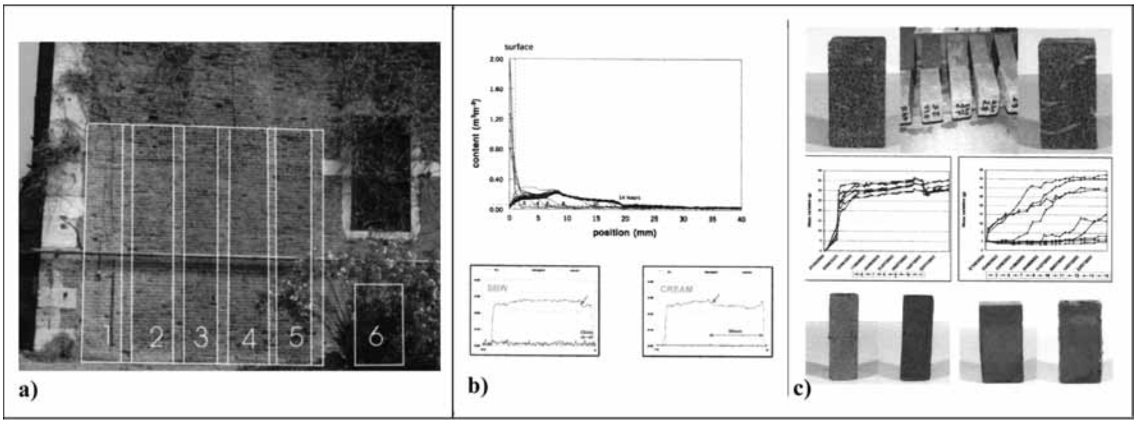

Figure 7: a) Case study of Torre Alberaria, Venice: location of treated zones; b) Laboratory and NMR analyses: measurements of penetration depth of different products on Dutch bricks and assessment of water adsorption; c) The dynamic simulator tests on Dutch brick show a remarkable mass variation of untreated bricks samples with open cracks while the treated reveals only a surface scaling, The graph of soft stone (Rhodes calcarenite) shows a different behavior concerning the loss of material between untreated and treated samples and, within the treated samples, a mass variation according to the pore size distribution

Also non-destructive controls (*Integrated Computerized Analysis of Weathering*) have been developed to investigate aspects related to the conservative treatment influence on samples of building material. The *I.C.A.W. technique* has been employed to detect in situ intrinsic anisotropic features (textural, elastic, mechanical) of the materials under investigations.

The results of the research indicate:

1) the possibilities and risks of treatments on salt loaded substrates emerge from compared analyses of the laboratory tests: i) it has been possible to assess the suitable products against sea-salt decay; ii) the identification of the suitable product for the conservative treatment depends, within the selected products, on granulometry and porosity of the different substrates.

Without the knowledge of the properties of the substrate on which the water-repellent can be applied, the laboratory tests performed demonstrate that the products are not always able to stop the liquid water transport even in the absence of salt (Fig. 8). Moreover, without specific information on the substrate, the following limits and possible risks connected to the application of water repellent treatments in masonry contaminated with NaCl are expected: i) the effectiveness (both penetration depth and water repellent effect) of the treatments, solvent based as well as silane cream, is drastically reduced when they are applied on a substrate with high NaCl load; ii) the salt crystallization damage can be enhanced by the application of water repellent treatment on a substrate already contaminated by NaCl: this happens not only in presence of rising damp in the wall, but may be already due to RH changes of the air. Damage development on substrates treated after salt contamination may be more severe than on untreated contaminated substrates, and favorable conditions for biological defacement may occur after treating salt loaded substrates (Fig. 9).

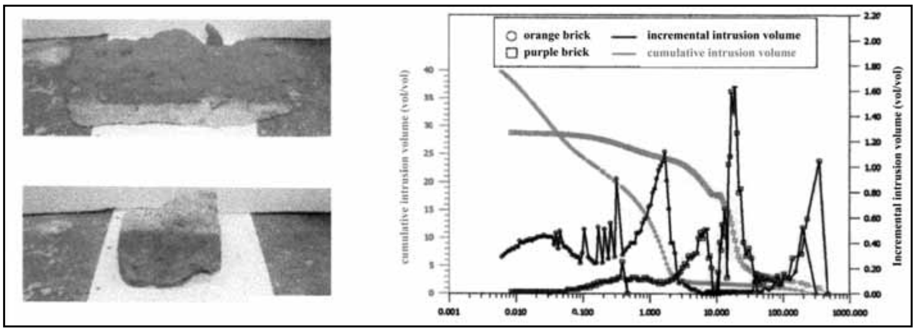

Figure 8: Difference in damage between bricks explained through their different pore size distribution

Figure 9: Sea-salt already present on treated substrate (a, soft calcarenite) provoking efflorescences (b) and scaling (c)

On the other hands, according the results of in situ investigations an evaluation of the products effectiveness can be expressed by the *protection degree* (Ep%), given by the following percent ratio: $Ep\% = (AD_{nt} - AD_t)/AD_{nt} \bullet 100$, where ADnt = Absorption Degree before the treatment; ADt = Absorption Degree after the treatment and $AD = (Q_{tf} - Q_{t5})$ /S in ml/cm^2 (Q_{tf} = amount of water absorbed at the end of the test, t_f = 30 min., in ml; Q_t = amount of water absorbed after 5 minutes from the start of the test, t_5 = 5 min., in ml; S = area of the Karsten-pipe). The Ep% was calculated after 1 month and 6 months from the application of the products. Data obtained comparing the results obtained before and after treatments, allow to establish that 1 month after the application the Ep% is over 80% for all the tested products, but six months after the application, this parameter is still so high only for Funcosil IC and Dynasylan BSM40SKI. The morphological observations and X-ray maps on the surface and on cross section of treated samples show different behavior of the applied products. For instance, as regards FUNCOSIL IC this product gives rise to a superficial film by deposition of silica gel with a maximum thickness of 10 µm. The observable pore-size reached is lower than 1 µm; sulphates have been soluted and subsequent precipitation take place forming submicronic crystals. Some round-shaped cavities are widespread distributed on fresh sulphate crust and distributions of chlorides and IC are superimposable on it. FUNCOSIL SNL forms a superficial film with a maximum thickness of 150 µm, the observable pore-size reached by the product is greater than 1 mm; in coarser pores (d > 20 µm) it settles as a random coil and does not form a coating. In the sample treated with RHOXIMAT HD RC80 it is quite evident a superficial film 8 µm as a maximum thickness; the minimum observable pore-size reached is 20 µm and in coarser pores the polymer forms a network of filaments. RHODORSIL RC90 gives rise to a superficial film 20 µm as maximum thickness; the observable pore-size reached is around 1 µm. In coarser pores it forms a superficial coating (~10 µm thick) often detached from the pore walls by salts. WACKER VP5035 form a superficial film, locally detached, which maximum thickness is 10 µm. The product reaches pores lower than 1 µm in size and penetrates into the salts crystals. SEM observation of sample treated with DYNASYLAN BSM40SKI reveals the presence of a superficial film of product 40 µm thick; the observable pore-size reached is higher than 10 µm but the treatment has a not homogeneous distribution inside the capillaries. Moreover, Funcosil IC gives rise to a superficial deposition of amorphous silica after treatment and it has a solvent effect on soluble salts reducing the dimensions of recrystallised salts. Rhodorsil RC90, Dynasylan BSM40SKI and Wacker VP5035 form an adherent film on pore walls while Funcosil SNL settles as a random coil. Furthermore bricks treated with RC90 show a detachment of coating due to salt crystallisation so it is not effective on contaminated substrates. Therefore, also the in situ tests showed that the water repellents are not always able to stop the liquid water transport even in absence of salt: the effectiveness depends on the type of product and on the substrate on which it is applied.

2) the decay patterns explain how to correlate the height of the rising damp zone with the salt distribution in the wall, distinguishing the zone subjected only to aerosol from the zone where the rising damp and, locally, sea flooding act. The previous diagnosis makes it possible to intervene in the zone affected by marine aerosol.

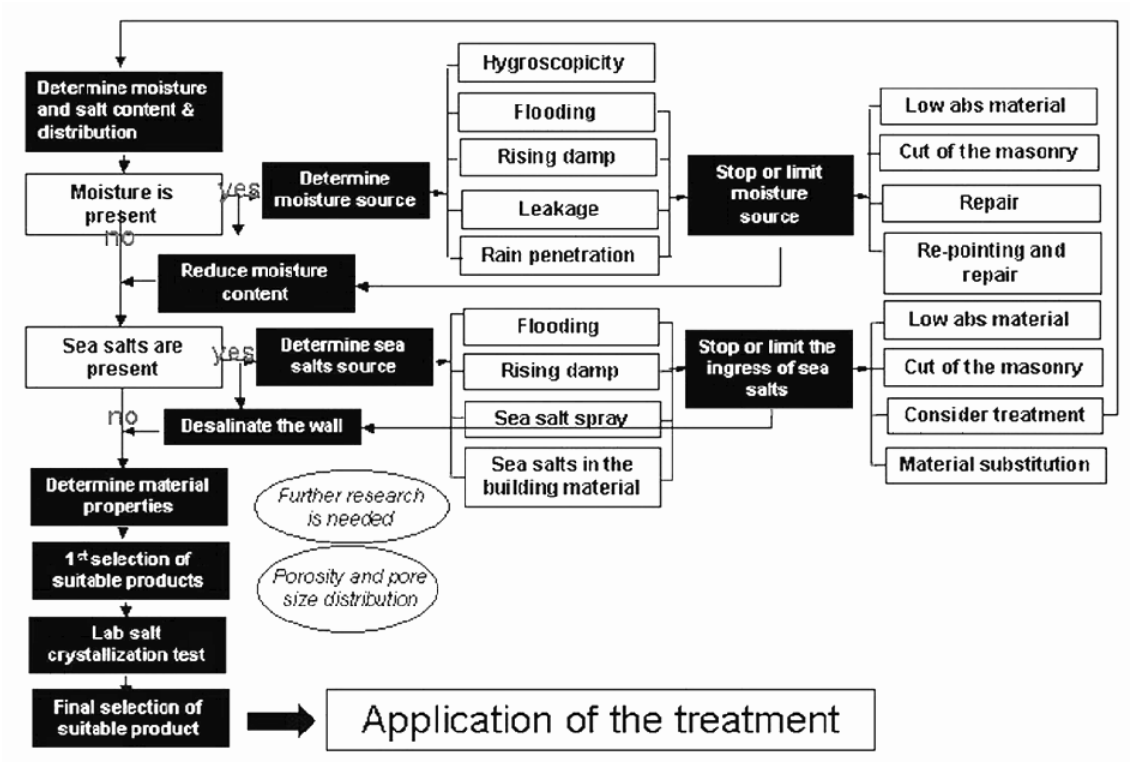

Figure 10: Criteria and methodology for treatment of walls affected by (sea) salts from ASSET

In the rising damp zone as well as in correspondence of sea flooding zone the assessment of different masonry morphologies with involved materials bring to focused on two interventions: i) desalination, because a too high salt load may lead to damage in case of treatments; ii) prevent further capillary rise of moisture and salts, as a preliminary consolidation of masonry and foundations by intervening with appropriate treatments at the base of the wall.

Taking care of protective treatments, such as water repellents and consolidants, may even lead to higher amounts of damage and faster decay, in the presence of salts it seems logical to verify as effective desalination may in many cases be the “conditio sine qua non” for this kind of treatments (Fig. 10-11).

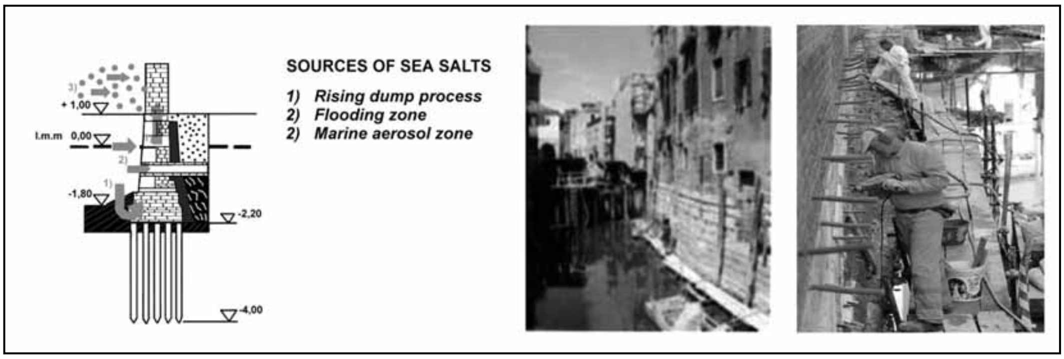

Figure 11: Intervention on masonry morphologies and foundation typologies affected by origin and spreading of sea-salt

3) an Expert System, the MDDS (*Masonry Damage Diagnostic System*) investigation techniques and methodologies, has been used within ASSET Project to give assistance in the diagnosis of the damage found in monuments and as instrument for knowledge dissemination. A Damage Atlas on specific matter was developed, including a new classification of the location of the damaged material(s), which was an effective way of grouping different types of damage, organized in relation to the materials affected, to study them in terms of location – source of salt – source of moisture. Knowledge derived from the in depth investigations carried out in the project was implemented in the System, aiming at making the consultations more complete and better meeting the users' need. Beside Sea-salt Damage Atlas, important papers, produced in the course of the ASSET project, were included as such in the 'Literature' section, to furnish the System and its users with a better theoretical support (Fig. 12).

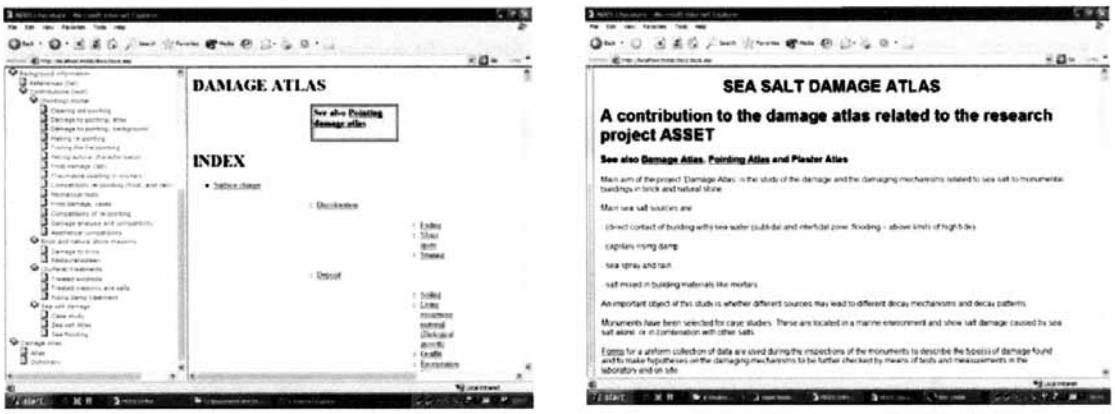

Figure 12: Examples of MDDS background information and the Sea-salt Damage Atlas with the new criteria inserted

2.2 DESALINATION Project

The Project uses the results and findings of the recently ended ASSET and also of the COMPASS project taking the available results into account in an optimal way. The ongoing DESALINATION Project is focused particularly on the assessment of desalination mortars and mortar / poultices for historic masonry (desalination).

An important aspect of desalination technique is the moisture and salt transport from the wall to the desalination system. A great deal is still not known about the effectiveness of these types of treatments and, in particular, the scientific basis to support the understanding of the processes involved is lacking. There are many factors that may influence the effectiveness of the extraction process, such as the amount of introduced water, the surrounding climatic conditions, the capillary properties of the poultice or mortar in relation with those of the substrate. Moreover, methods to assess the likely behavior of residual salts remaining after treatment are currently not available. This makes the situation for the end-users, with respect to the choice of an appropriate desalination system, extremely difficult to interpret.

The main aim of this project is to provide those responsible for the care and maintenance of the built cultural heritage (architects and advisors, and also owners and heritage authorities) with clear guidelines for an adequate choice of a desalination system for building materials**.** The second aim is to gain scientific knowledge on how desalination works, to be able to help European SME's in product development.

Central scientific and technical objectives in the project are: i) gaining a better understanding of the salt transport mechanism between a salt laden substrate and a material applied on top of that; ii) assessing the possibilities and limitations of desalination treatments.

The core of the project is the assessment of desalination systems on wall and finishes in monumental buildings and their impact on these monuments. Key questions to be answered in this respect are to what extent is the desalination method effective to remove damaging salts from the monument and if the desalination methods themselves may have any negative effects on the historical materials used in the monument.

The project is subdivided in several work packages. It is foreseen a work package to gain more insight in nowadays desalination in practice. A list of desalination systems used in the participating countries will be one of the deliverables.

Investigations, including non destructive techniques (NDT) will be carried out through case studies: to define the quantitative assessment of any discoloration caused by the desalination process (*color measurements*); to identify modifications of the surface morphology of the treated surfaces (*micro-morphological evaluation*) at different degree of magnification (*stereomicroscopy*); to investigate micro-crypto crystalline aggregates (*polarizing microscopy*); to investigate the presence of salts trapped within the substrate porosity (*SEM analysis*); to evaluate water and salts contents (*georesistivimeter*) before and after treatment application (*infrared thermographic analyses*).

Information deriving from the case studies such as salt load on types of substrate will be used in laboratory tests regarding the performance of desalination systems. The objectives of these tests are a) to gain knowledge about the behavior of different desalination systems on different substrates, b) to select mortars / poultices, c) to design a test to evaluate the performance of desalination systems, d) to design a scheme which indicates what desalination system may be used successfully on substrates with specific pore-size distribution (= formulate guidelines).

The experiments will start with two extremes, one very fine porous (calcium silicate brick) and one very coarse porous (Bentheimer sandstone) substrate. The tests will be carried out using different types of salt: chlorides, sulfates, nitrates and mixtures of the salts mentioned. On the different substrate-mortar / poultice combinations, the following parameters will be take into account: drying time of mortar / poultice; way of binding of the salt in the mortar / poultice; drying shrinkage of mortar / poultices; workability; thickness of mortar / poultice; thermodynamic behavior (with respect to relative humidity and temperature) of the salt systems present before and after treatment.

The performance of the desalination system will be determined by measurement of the following: amount of salt accumulated in mortar / poultice; influence of the type of salt on desalination; depth of desalination (by measuring hygroscopic moisture content); influence of desalination treatment on the behavior of salt systems present with respect to relative humidity and temperature; influence of a filter between substrate and mortar / poultice to protect fragile substrates (Fig. 13).

This research will be carried out using, among others, the following techniques: salt and moisture distribution in substrate by hygroscopic moisture content; salt distribution in mortar / poultice by chemical analysis; thermodynamic modeling of salt behavior; binding of salt in mortar / poultice by extraction and ESEM.

This evaluation should answer questions like "how many salts can be extracted from a given substrate?", "what is the depth of desalination?" and "what transport mechanism is the most important with respect to desalination?". To answer the last question and to thoroughly study the transport of moisture and salt between substrate and desalination system using Nuclear Magnetic Resonance (the NMR-scanner), there will be a close cooperation between partners involved in laboratory tests.

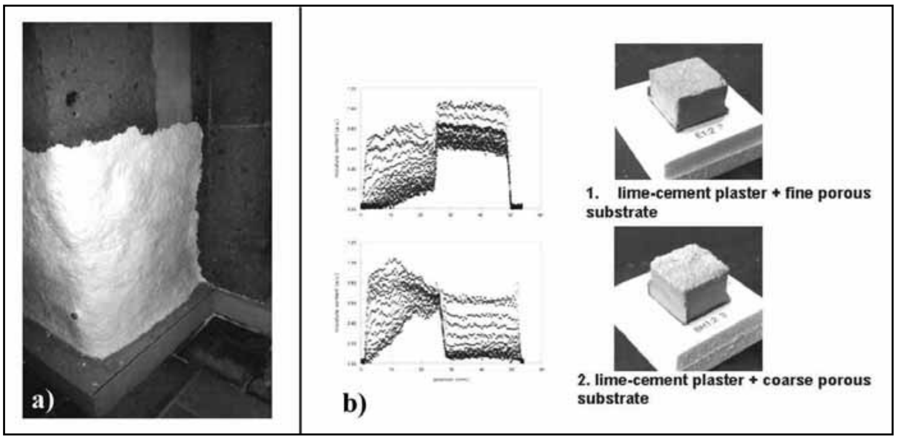

Figure 13: Desalination Project methodologies: a) poultice applied on salt loaded column in Drachenfels Trachyte (Cologne); b) drying behavior of plaster – substrate systems (from Compass Project): model for desalination

The project will result in new knowledge about the way desalination works and the basic requirements for new desalination methods. Also a standard test method for desalination will be developed. One of the main results of the DESALINATION project will be a clear guideline on how to come to a choice of desalination system. This is of much importance to the European decision makers and will be incorporated in a knowledge based decision tool. The use of better desalination system forms a clear step forward to a durable approach of maintenance in the cultural heritage.

3 Conclusions

To improve the desalination systems, more scientific knowledge on the transport mechanism of desalination as well as practical methods to assess the quality of desalination are needed. The standard test to be developed in this project will increase possibilities to judge and compare desalination systems, which will help in product development. The research fits in the European initiative towards standardization in the field of Conservation of Cultural Properties.

European companies, including SME's, are world leaders in the field of conservation products, treatments and conservation practices. They have the advantage of a long history of conservation actions because of the large presence of monuments in Europe, a tradition of continuous innovation of products and methods and possess high skills and craftsmanship. This project will contribute to the increase of their competitiveness not only on their European home markets but also on other markets.

In DESALINATION project enterprises involved in development and production of conservation treatments, restoration planning and practices are participants. New knowledge will be available for them, especially on a topic like the working principles of desalination. Together with the new standard test the companies can create a competitive advantage. Knowledge will however be disseminated to end-users, so to enhance a broader uptake of results. Desalination methods will be assessed, new scientific knowledge obtained and a new standard test proposed. This will contribute to the quality of the methods applied and therefore to the quality of the preservation of monuments subjected to these treatments. In this respect the project will greatly improve preservation strategies for monumental buildings, decreasing or even stopping further deterioration. It will conduct to a sustainable cultural heritage in which less maintenance is needed and replacement of material will be less frequent. To stop monument weathering and come to preservative action is a key issue in the EU policy for preserving the European cultural heritage as is set down in the 'European Spatial Development Perspective (1999) and the 'community Action Plan in the field of Cultural Heritage' (Council decision OJ 94/C 235/01). In this respect can be mentioned the 'Culture 2000-Programme'. This programme shall contribute to the promotion of a cultural area common to the European peoples. Moreover, one of the specific objectives of the Project is disseminating know-how and promoting good-practices concerning cultural heritage conservation and safeguarding. Within this programme one of the actions to be undertaken is to enhance cultural sites and monuments within the community with a view to raising awareness of European culture. The Desalination project will support this enhancement, particular of monuments, by stopping damaging actions of salts and make better and sustainable preservative actions or restorations possible.

End-users such as manufacturers, architects, monument owners and heritage authorities will be kept carefully and regularly informed on the project progress and results. The knowledge gained will lead to a better judgment of practitioners on how to choose an adequate desalination system and it is expected to give an impulse to product development. Indeed, one of the main results of DESALINATION project will be a clear guideline on how to come to a choice of desalination system. This is of much importance to the European decision makers and will be incorporated in a knowledge based decision tool. The use of better desalination system forms a clear step forward to a durable approach of maintenance in the cultural heritage, while a better knowledge of moisture and salt transport from the historic material to the desalination product will give raise to a recommendation for a test to assess the effectiveness of desalination products. Therefore, in order to create a guideline, the following goals have to be reached: a) formulation of a method to assess a performance of desalination systems; b) scientific knowledge on how desalination works, to be used in product development by European SME's; c) recommendation for a new standard to test desalination systems; d) decision-guideline how to choose a desalination mortar / poultice.

4 European project details

ASSET, Contract No. EVK4-CT 2000-0023, Assessment of suitable products for the conservative treatments of sea-salt decay.
Co-ordinator Prof. Fulvio Zezza.
Affiliations: University IUAV of Venice-CUM School Monument Conservation, Italy; Building and Construction Research, Dept. Division Building Technology (TNO), The Netherlands; University IUAV of Venice-DSA, Italy; Laboratoire de Constructiòn Civile et Maritime, Université de La Rochelle (ULR), France; associated contractors: Eindhoven University of

Technology, Dept. Applied Physics (EUT), The Netherlands; Remmers Bouwchemie B.V. – Hoogeven (REM) The Netherlands; sub-contractor: Istituto Veneto Beni Culturali (IVBC), Italy.
DESALINATION, Contract No. 022714, Assessment of Desalination Mortars and Poultices for Historic Masonry.
Co-ordinator Prof. Fulvio Zezza
Affiliation: University IUAV of Venice, Italy; TNO Built Environment and Geosciences, The Netherlands; Cercle des Partenaires du Patrimoine (CPP) with the Laboratoire de Recherche des Monuments Historiques (LRMH), France; Eindhoven University of Technology, Dept. Physics (EUT), The Netherlands; Fachhochschule Koeln, University of Applied Science Cologne (UASC), Germany; Remmers Bouwchemie B.V. (Remmers), The Netherlands; Rijksgebouwendienst, Government Building Agency (RGD), The Netherlands; Enterprise Quelin, France; E. Pallot, Compagnie des Architectes en Chef des Mon. Historiques (ACMH), France; J. Paul Getty Trust (GCI), USA.

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Hygric dilation behaviour of NaCl contaminated lime-cement mortar

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Key words: NaCl, hygric dilation, salt crystallization, salt damage

Abstract
The mechanism of damage occurring in NaCl contaminated building materials has not been clarified yet. Apart from crystallization pressure, other theories have been proposed to explain the cause of serious decay observed in practice. In this research the hypothesis that damage may develop due to the irreversible dilation occurring during crystallization of the salt is considered. Aim of the study is to contribute to the modeling of this phenomenon, not unequivocally described yet, for lack of targeted experiments on a conspicuous number of materials.

The experiments performed on a lime-cement plaster indicate that NaCl modifies the hygric dilation behavior of a material completely. The plaster contaminated with NaCl shrinks during dissolution and dilates during crystallization of the salt. This dilation is irreversible and its amount is sufficient to damage the material after few dissolution / crystallization cycles. This behaviour is not restricted to NaCl, but has been observed for other salts as well ($NaNO_3$ and KCl).

When a crystallization inhibitor, modifying crystallization habits of the salt, is added to the NaCl, no irreversible dilation is measured anymore and no damage occurs even after several dissolution / crystallization cycles.

Outcomes of electron microscopy studies suggest that a relation exists between crystallization habit of the salt and dilation behaviour. Salts crystallizing as a layer adhering to the pore walls seem able to strongly affect the hygric dilation of the material producing relevant expansion during drying of the specimen and crystallization of the salt. This effect is, in this theory, not possible when the same salt crystallizes without adhering to the material, as in the presence of the crystallization inhibitor.

This research has been developed in the framework of the EU project COMPASS (Compatibility of Plasters and Renders with salt loaded substrates in historic buildings – EU Contract no. EVK4-CT-2001-0047-DGXII, www.compass-salt.org), which studied the compatibility of plasters when applied on salt loaded substrates.
Part of the results reported in this paper has been published in [17].

1 Introduction

Salt crystallization is a frequent cause of decay of building materials. In spite of the several theories developed, no unanimous opinion exists yet on the salt damage mechanism. The situation is even more controversial in the particular case of NaCl. According to the most accepted model [1, 2, 3], salt crystallization damage occurs because salt fills the pores and creates pressure on the pore walls. This pressure is dependent on the supersaturation ratio. In an equilibrium situation, the degree of supersaturation that can be reached depends on the pore radius: the smaller the pores, the higher the supersaturation. Following this theory, in order to produce crystallization pressures high enough to cause damage, NaCl should crystallize at high supersaturation, filling pore sizes in the range of a few nanometers [4, 5].

Some objections have been raised to the possibility of NaCl to develop high pressures: NaCl has a low tendency to supersaturate [6, 7], therefore it would not be able to produce high crystallization pressures. Besides, most traditional porous building materials do not have pores in the nanometer range. Nevertheless they may show serious damage in the presence of NaCl. Recently the hypothesis of crystallization in a non-equilibrium situation (e.g. in case of fast evaporation), and the possible development of high crystallization pressures even in larger pores, has been suggested by [8, 7], but no experimental proof of this theory has been given yet.

The discussion reported above suggests that damage due to NaCl may not only be related to crystallization pressure as described in literature starting with Correns' work, but involves other mechanisms too. Some authors [9, 10, 11] have observed that NaCl strongly affects the dilation behaviour of some materials (sandstone containing clay and brick) but no definitive explanation for this mechanism has been given yet. An important reason that hampers the clarification of this possible damage mechanism is the lack of systematic experimental investigations of the phenomenon. Until now, only few experiments have been carried out on a restricted number of materials.

The research reported in this paper is aimed at studying the dilation phenomenon in detail and at verifying it for different salt types. The research was performed on lime-cement mortar specimens. The experiments were carried out in steps:

- the effect of NaCl on the hygric dilation behaviour of the lime-cement mortar was investigated;
- the dilation in the presence of $NaNO_3$ and KCl was studied in order to check whether the observed behaviour was limited to NaCl or common to more salts. These two salts were selected because they are both hygroscopic, they do not have hydrated forms and each of them has one ion in common with NaCl;
- the effect of a crystallization inhibitor, modifying the crystal habits of the salt, on the dilation behaviour of NaCl contaminated specimens was investigated.

2 Materials and method

A lime-cement mortar has been selected for this study. This mortar has been shown to be extremely susceptible to damage due to sodium chloride [12]. The most relevant properties of this mortar are reported in Table 1. The pore size distribution measured by Mercury Intrusion Porosimetry (MIP) is bimodal with most of the pores in the range 0.1-1 μm and 40-80 μm.

Table 1: Physical and mechanical properties of the lime-cement mortar

Binder	Aggregate	Lime:cement :aggr. ratio	Water content (% by mass)	Total porosity (vol%)	Mechanical strength*** (N/mm^2)	
					Flexural	Compressive
hydrated lime + cement	siliceous (grain size 0.5-1 mm)	4:1:20	20	32.3* 27.4-27.8**	0.1	0.3

* as measured by immersion according to [Klu94]
** as measured by MIP
*** the mechanical strength was measured according to the EN 1015-11; a loading rate of 5 N/sec and 50 N/sec was applied in the bending and compressive test, respectively

Mortar specimens with a size of 20 × 10 × 2 cm were used for the study of hygric behaviour. The mortar slabs were prepared on a brick substrate from which they were detached after one day. A filter paper was used between the substrate and the plaster to facilitate the detachment. The lime-cement mortar specimens were stored at 20 °C 65% RH for 2 weeks, and subsequently dried at 30 °C for 2 days and carbonated in a cabinet at 20 °C 50% RH and 0.3% CO_2. After 15 days the complete carbonation of the specimens was checked by spraying with phenolphthalein at freshly broken cross section.

Before measuring the hydric and hygric behaviour the specimens were contaminated with NaCl according to the following procedure: the mortar slabs were sealed on the four lateral sides by epoxy resin and a NaCl saturated solution (concentration 6M) was introduced from the bottom by capillary rise (figure 1). An amount of solution equal to the Capillary Moisture Content (C.M.C.) of the mortar (i.e. the moisture content high enough to wet the upper surface) and leading to 2% m/m of NaCl in the specimen was used. This amount of salt has been proven to be enough to damage this material [12 Studies in Conservation]. After contamination, the specimens were sealed at the bottom with removable tape and dried at 10% RH and 20 °C until a constant weight was reached. This drying process led to almost no efflorescences; salts accumulated just beneath the evaporation surface of the specimen. Since the crystallization inhibitor increases the tendency of the salt to efflorescence, the specimens contaminated with NaCl plus inhibitor were dried at 40 °C. By the use of a high temperature the drying front recedes fast in the material preventing the formation of efflorescences. Once the specimens contaminated with salt had dried, metal supports for the Linear Variable Differential Transformer (LVDT) to be used in the measurement of the hydric and hygric behaviour were glued on the evaporation surface of the mortar slabs. The supports were glued, by means of a two-components glue, at a distance of 150 mm from each other (figure 2).

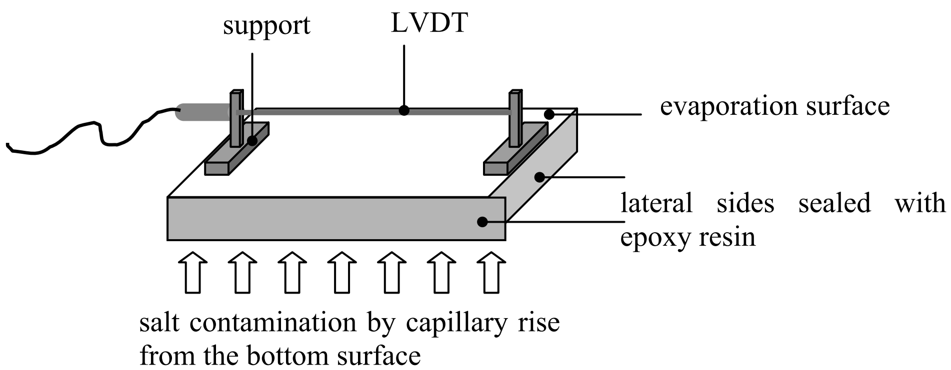

Figure 1: Salt contamination of the specimen

The hygric behaviour of the specimens was monitored inside a climatic cabinet in which the temperature and RH of the air can be programmed and controlled. In order to reach a very low RH, dry air was blown into the cabinet. The measuring apparatus (figure 2) was composed of:

- a balance with an accuracy of 0.1 g, connected to a PC, for monitoring the variation in specimen weight due to hygroscopic moisture uptake and release, connected to a PC; in some of the experiments two balances were used;
- a LVDT fixed to the supports glued on the mortar and connected, through the data acquisition system Labview, to a PC;
- two data loggers for a double check of the temperature and RH of the air in the climatic cabinet.

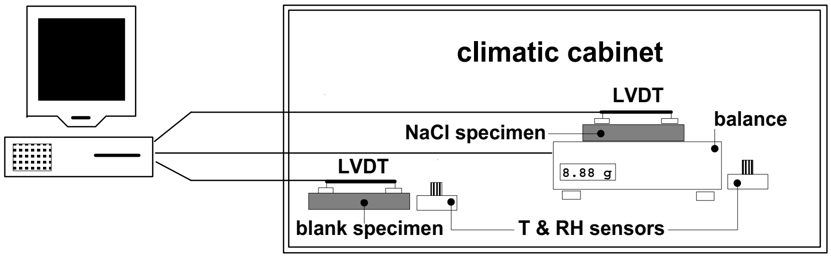

Figure 2: Test set up: the specimens, on which the LVDT's are mounted, are placed in a climatic cabinet. A PC collects the data on the dilation and on the mass changes. Temperature and RH sensors are used for an additional check of the environmental conditions

3 Results

3.1 Hygric behaviour of NaCl contaminated specimens

The hygric behaviour of NaCl contaminated and blank (reference) mortar slabs was measured. The specimens were placed in the climatic cabinet. The temperature was maintained constant at 20 °C and the RH was varied between about 10% RH and 90% RH every 48 hours. Six RH cycles were performed. During the test the NaCl contaminated specimen was put on a balance and its mass was continuously monitored. The results, reported in figure 3, show that the blank specimen dilates during the high RH period and shrinks during the low RH period, as expected [Hil64], while the NaCl contaminated specimen behaves in the opposite way. The dimensional changes of the salt contaminated specimen are not only opposite but also much larger than for the blank specimen. When the cycles are repeated, the dilation increases while the shrinkage remains about the same magnitude: this leads to an increasing and irreversible dilation that reaches, at the end of the sixth cycle, 1.3 µm/mm. On the contrary, the dimensional changes are completely reversible for the blank specimen. The dilation leads to a stress that is likely to exceed the low tensile strength of the plaster and in fact results, at the end of the test, in serious damage. The damage consists of sanding of the outer layer of the plaster; the material loss is about 7% of the initial mass of the specimen. The serious damage observed points out the importance of RH changes for the development of the salt decay in lime-cement mortars. The results obtained in this work are in accordance with the data reported in the literature for clay containing sandstone and for brick [9, 11]. Moreover, the experiments on the lime-cement mortar clearly demonstrate that the presence of reactive clay is not a necessary factor for the dilation behaviour observed in NaCl contaminated materials.

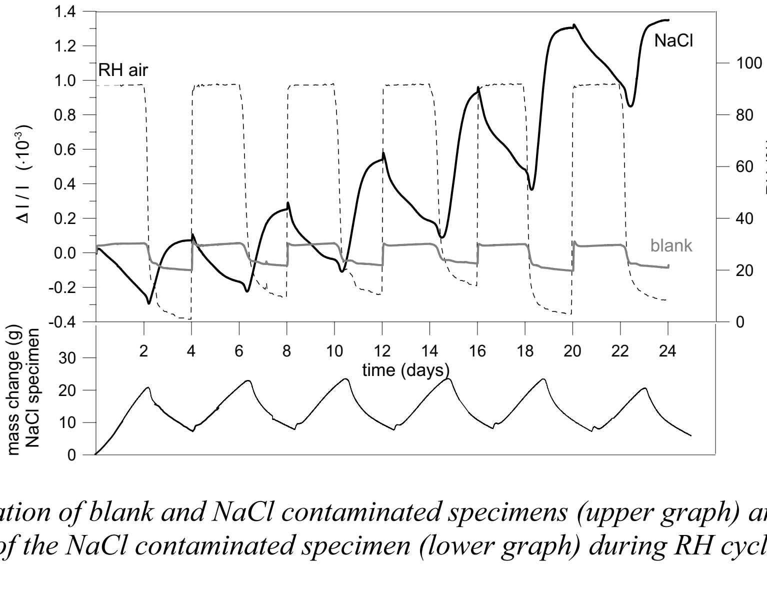

Figure 3: Dilation of blank and NaCl contaminated specimens (upper graph) and mass change of the NaCl contaminated specimen (lower graph) during RH cycles

In order to obtain a better understanding of the dilation mechanism, more detailed experiments were necessary. Performing a RH cycle slowly and with small increments would allow identifying the point at which dilation and shrinkage occur and relate these processes unequivocally to either salt crystallization or dissolution. A new experiment was set up in which the RH was varied stepwise between 30 and 96% RH. Each step in RH was done in 1 hour and was followed by 23 hours at constant RH. The experimental data (figure 4) clearly show that the blank specimen dilates while the RH increases and shrinks while the RH decreases. On the other hand, the NaCl contaminated specimen shrinks at RH values higher than 75% and considerably dilates when the RH drops below 75%. Three parts can be distinguished in the curves:

1. *Increasing the RH in a region below the RH of equilibrium of NaCl (30-75% RH)*
In this RH range the behaviour of the blank and of the NaCl contaminated specimens is similar: both dilate when the RH increases. The dilation is due to water vapour adsorption [13].

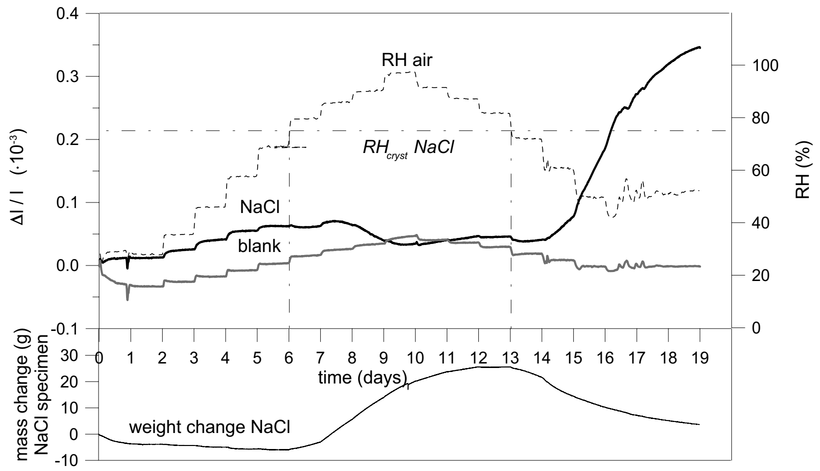

Figure 4: Dilation of blank and NaCl contaminated specimens (upper graph) and mass change of the NaCl contaminated specimen (lower graph) during a single RH cycle (max RH 95%)

2. *Increasing and decreasing the RH above the RH of equilibrium of NaCl (75-96-75% RH)*
After crossing the value of 75% RH, the behaviour of the NaCl contaminated specimen starts to deviate from the specimen without salt: as soon as liquid water is present in the plaster (as shown by the mass change), the salt starts dissolving and some shrinkage is measured. The shrinkage of the salt contaminated specimen during salt dissolution is probably due to the release of the tension developed during the crystallization that occurred during the initial contamination of the specimen. A definitive proof of this hypothesis is given in section 3.2.

3. *Decreasing the RH (75-45% RH) below the RH of equilibrium of NaCl*
When the RH drops below 75%, the salt contaminated specimen starts drying (as shown by the mass loss) and dilates considerably. The curve becomes steeper with decreasing RH. At the end of the test, after 4 days of drying, the measured dilation is about 0.35 µm/mm. The non-contaminated specimen shrinks, as expected, when the RH is lowered; at the end of the cycle it has returned to its original length.

A further proof that the behaviour of a salt contaminated specimen is modified only if the equilibrium RH of the salt is crossed, is given by another experiment in which the RH was varied but kept below 75% (figure 5): in this case no irreversible dilation took place. The changes in length of the blank and of the NaCl contaminated specimen are similar, moderate and reversible.

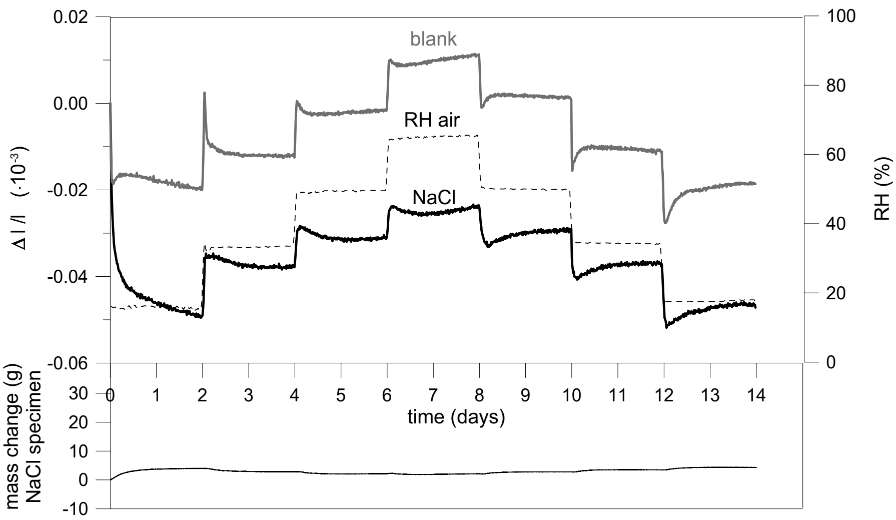

Figure 5: Dilation of blank and NaCl contaminated specimens (upper graph) and mass change of NaCl contaminated specimen (lower graph) during a RH cycle below 75% RH

3.2 Effect of absorption of NaCl solution on dilation

In order to prove that the shrinkage measured during dissolution of the sodium chloride is due to release of the stresses developed during the crystallization of the salt that occurred during the initial contamination of the specimen, the following experiment was set up. Solid NaCl (2% of the dry weight of the specimen) was distributed over the surface of a mortar slab not previously contaminated with salt. The specimen, with the LVDT attached to it, was placed in the climatic cabinet and the RH was increased over the RH of equilibrium of NaCl (75%). This caused the dissolution of the salt and the absorption of the salt solution in the specimen. The absorption of the salt solution resulted first in dilation of the specimen (figure 6). Then the RH was lowered and the salt crystallized producing additional dilation. When the RH was increased again over the RH of equilibrium and the salt dissolved, the specimen shrank. This experiment clearly demonstrates that the shrinkage occurring during dissolution of the salt is due to the release of the stresses produced during crystallization. If dissolution of the salt takes place in specimens in which no crystallization event had occurred before, no shrinkage is measured.

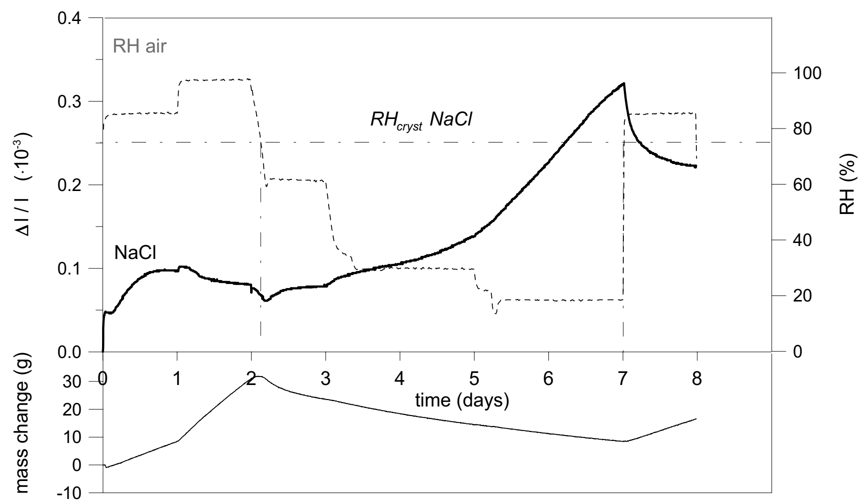

Figure 6: Change in length of a blank specimen during absorption of NaCl solution, subsequent crystallization and re-dissolution of the salt

3.3 Hygric behaviour of $NaNO_3$ and KCl contaminated specimens

The above-described experiments have shown that NaCl is able to produce irreversible dilation during crystallization. To check whether this behaviour is specific for NaCl or occurs also in the presence of other salts, further experiments were set up.

Two hygroscopic salts were selected having a cation or anion in common with NaCl, respectively, and no hydrated forms: $NaNO_3$ and KCl. The specimens were prepared in the same way as with NaCl. The same amount of solution was introduced in the mortar. The concentration of the solution was defined in such a way as to reach a salt content of 2% of the mass of the dry specimen in all cases.

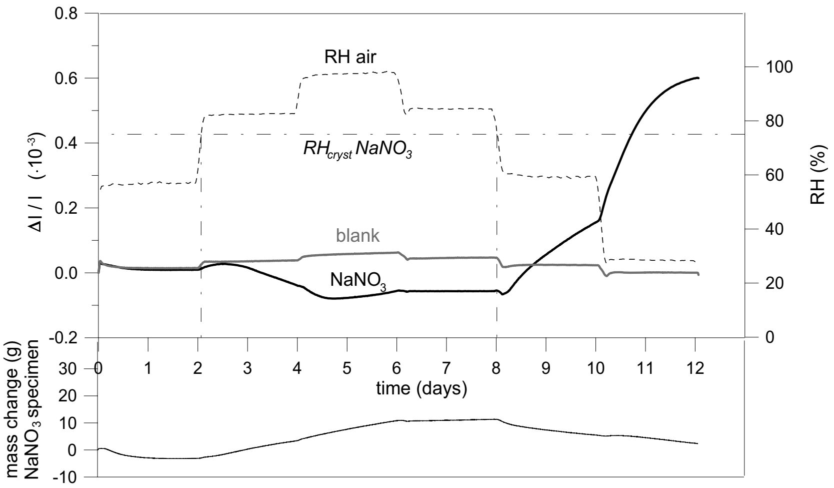

Figure 7: Dilation of blank and $NaNO_3$ contaminated specimens (upper graph) and change in mass of the $NaNO_3$ contaminated specimen (lower graph) during a RH cycle

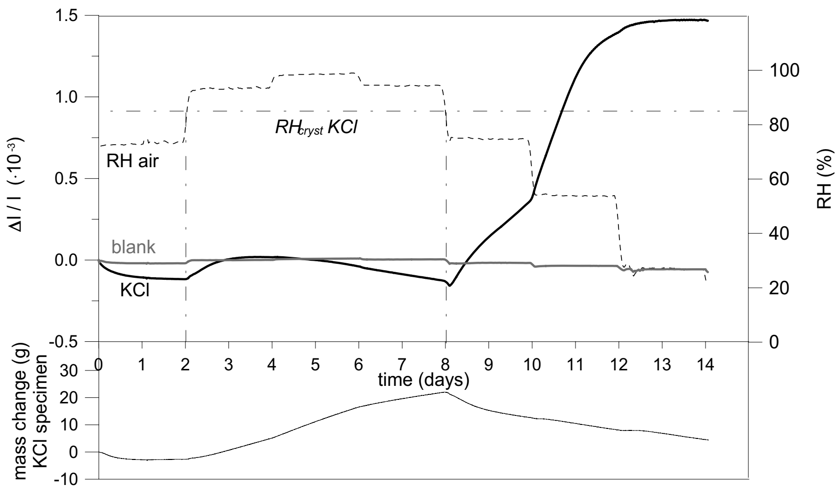

Figure 8: Dilation of blank and KCl contaminated specimens (upper graph) and change in mass of the KCl contaminated specimen (lower graph) during a RH cycle

As shown in figures 7 and 8, in both cases shrinkage is observed when the RH exceeds the values where water starts to condensate and the salts dissolve in the water (at 20 °C this happens at 85% and 75% for KCl and $NaNO_3$, respectively [14]. When the RH decreases below these values the specimens start drying, the salts crystallize and dilation occurs. Therefore it can be concluded that this behaviour is not typical for NaCl but it is common for more salts.

3.4 Hygric behaviour of NaCl contaminated specimens in the presence of a crystallization inhibitor

The use of crystallization inhibitors may help answering some questions about the damage mechanism, because these products are supposed to increase the supersaturation level (and therefore the theoretical crystallization pressure) at which salt crystallization occurs and to modify the crystal habits [15]. In the present study sodium ferrocyanide ($Na_4Fe(CN)_6 \cdot 10H_2O$) has been chosen because it has been shown to be very effective in inhibiting NaCl crystallization [15].

Two mortar specimens were contaminated with a NaCl saturated solution, with 0.1% (m/m) and without sodium ferrocyanide, $Na_4Fe(CN)_6 \cdot 10H_2O$. In both specimens the same amount of NaCl was introduced. The specimens were then placed in the climatic cabinet and the RH was varied step by step between 30% and 98% RH. In figure 9 the measured dilations are plotted as well as the mass change of the specimen containing the inhibitor.

The specimen contaminated with NaCl solution shows, as expected, significant dilation during drying. The specimen with NaCl plus inhibitor displays, surprisingly, no change in length at all. The almost complete drying (and therefore the occurrence of salt crystallization) of the specimen containing the inhibitor can be checked by looking at its mass at the end of the experiment. The absence of significant shrinkage during dissolution of the salt in the presence of the inhibitor, suggests that hardly any tensions have been developed in this specimen during the crystallization of the salt following the initial contamination with salt solution.

In order to study the long-term effect and the consequences of the presence of the inhibitor on the damage, an experiment comprising repeated RH cycles between 20% and 88% RH was performed. The results are plotted in figure 10. The specimen containing the inhibitor dilates during the high RH periods and shrinks during the low RH periods. The changes in length slightly increase with cycling. However, at the end of the experiment no irreversible dilation has occurred. The behaviour of the specimen contaminated with NaCl is completely consistent with the results reported before, showing an irreversible and increasing dilation during subsequent crystallization cycles of the salts.

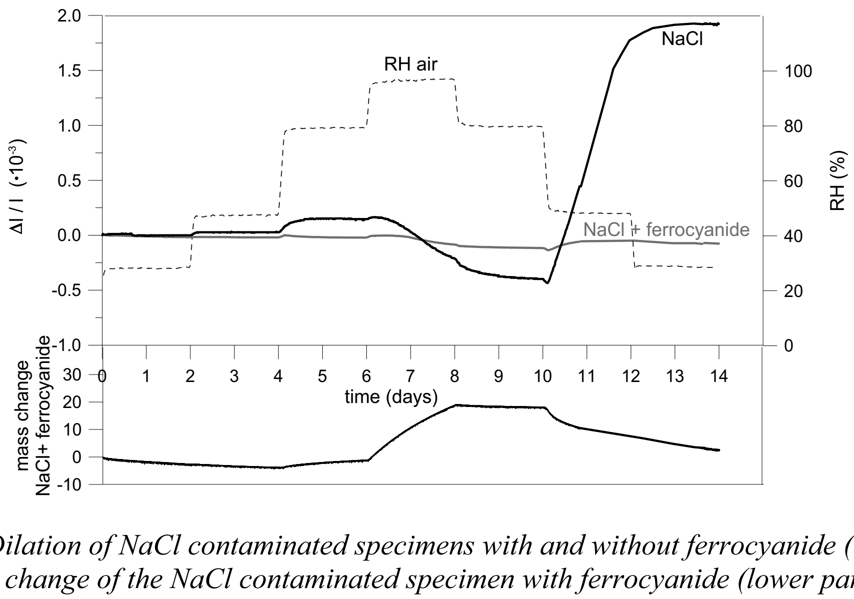

Figure 9: Dilation of NaCl contaminated specimens with and without ferrocyanide (upper part) and mass change of the NaCl contaminated specimen with ferrocyanide (lower part) during a RH cycle

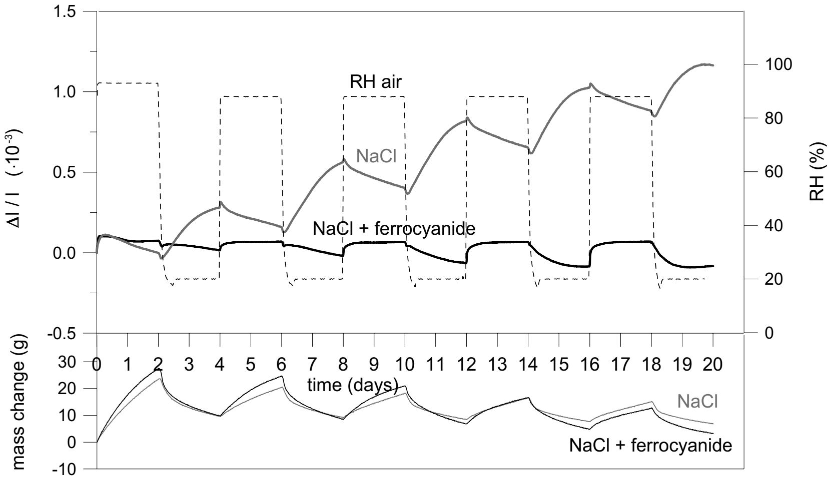

Figure 10: Dilation (upper part) and mass change (lower part) of NaCl contaminated specimens with and without crystallization inhibitor during several RH cycles

In spite of the similar amount of adsorbed / evaporated water in presence and absence of the inhibitor, strikingly different dilation behaviour is observed. This corresponds to the difference in damage observed at the end of the experiment. The specimen contaminated with pure NaCl showed sanding of the surface layer. The specimen containing the inhibitor did not suffer any visible damage. This is surprising because, according to the theory relating crystallization pressure to the level of supersaturation, the higher level of supersaturation reached in the presence of the inhibitor should result in a higher crystallization pressure and, therefore, in more severe damage. However, for crystallization pressure to be developed, the salt should grow filling confined spaces [1]. The question arises whether the latter is the case in the presence of the inhibitor.

3.5 ESEM investigations

Environmental Scanning Electron Microscopy (ESEM) has been performed on the specimens subjected to RH cycles, after their complete drying. The cross sections of the outer layer (about 3 mm thick) of mortar specimens before and after the test described in the previous sections, were studied using a Back Scattered Electron (BSE) detector. The composition of the salt crystals was checked with Energy Dispersive Spectroscopy X-ray Microanalysis (EDX). The investigations aimed to study the crystallization pattern of the salt, i.e. the habits and the location in which the salt crystallizes in the pores.

In the ESEM picture of a broken cross section of lime-cement mortar contaminated with NaCl, the salt is visible in large pores, creating a layer over the pore walls (figures 11a,b). It looks as if a good adhesion exists between the material and the salt crystals. This behaviour of NaCl is in accordance with other recently reported observations [16]. Below the salt, most of the distinguishable pores appear to be empty (figure 11c).

The presence of a salt layer covering and partially filling large pores was also observed for $NaNO_3$ (figure 12a) and KCl (figure 12b).

The addition of ferrocyanide to the NaCl solution changes the crystallization pattern of the salt. The NaCl does not show a strong affinity to the substrate anymore: it does not cover the pore walls in the form of a layer, but crystallizes mainly as an agglomerate of crystals, not attached to the material (figure 12c). The crystallization pattern does not change significantly after repeated RH cycle.

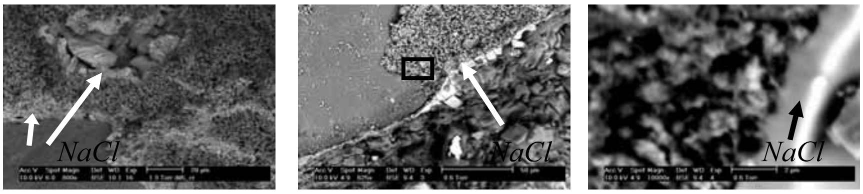

Figure 11: ESEM photomicrographs showing NaCl (lighter areas) crystallizing as a layer adhering to the binder and partly filling large pores (a-b); next to the salt layer (white area), pores not filled with salt are visible (c)

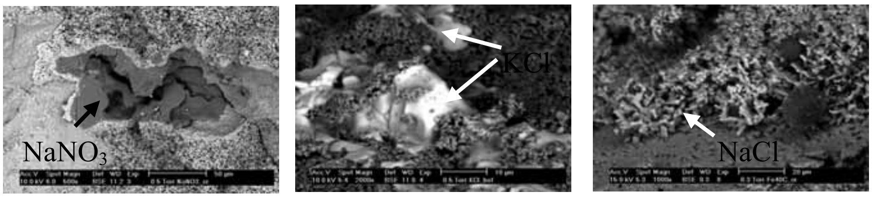

Figure 12: a) ESEM photomicrograph showing $NaNO_3$ crystallizing as a layer on the pore wall
b) ESEM photomicrograph showing KCl crystallizing as a layer on over the pore wall
c) ESEM photomicrograph showing NaCl crystallization in the presence of an inhibitor

4 Discussion and conclusions

The reported experiments unambiguously prove that the presence of NaCl modifies the hygric dilation of a material completely, even in absence of reactive clay. In a non-contaminated lime-cement mortar, dilation occurs when the RH increases and shrinkage when the RH decreases. In lime-cement mortar contaminated with NaCl the opposite happens: dilation is measured during the drying phase of the RH cycle, when the salt crystallizes; shrinkage is observed during dissolution of the salt. It has been unequivocally demonstrated that the dilation is due to crystallization of NaCl. In fact it only occurs in the presence of the salt, when the RH of the air is low enough to cause the evaporation of water. The dilation is irreversible and leads, when more cycles are repeated, to damage.

The different dilation behaviour between salt contaminated and blank specimens suggests that shear stresses may develop in a salt contaminated material because of the differential dilation of areas containing different amounts of salt. This theory may explain those cases of damage in which there is no evidence of salt filling spaces under detached scales or layers.

The dilation behaviour observed in NaCl contaminated lime-cement mortar has also been verified for other hygroscopic anhydrous salts ($NaNO_3$ and KCl), showing that this phenomenon is not restricted to NaCl but it is common to more salts.

In the case a crystallization inhibitor is added to the NaCl solution, neither dilation nor damage occurs. The ESEM observation has shown that absence of dilation corresponds to a different crystallization pattern of the salt: NaCl, instead of crystallizing as a layer on the pore walls, forms, in the presence of the inhibitor, agglomerations of crystals not adhering to the substrate.
These results lead to a new hypothesis on the salt damage mechanism based on the mechanical interaction between salt and pore wall. Salt crystallizing as a layer appears able to transfer stresses to the pore walls and thereby to cause dilation; this effect does not occur when salt crystallizes without adhering to the material, as in the case the inhibitor is added.

The absence of damage in presence of the inhibitor suggests the possible practical applications of these products for the prevention of salt decay. The possibilities and the risks connected to the use of crystallization inhibitors in building materials are at the moment investigated in the framework of the EU project SALT CONTROL (Prevention of salt damage to the built cultural heritage by the use of crystallisation inhibitors, EU Contract no. 501571, https://salt.ugent.be).

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Archaeometry and the Nabatean mortars

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Abstract
Within the three years of the duration of the NAMO (Nabatean Mortars – Technology and Application) project a research team tried to learn and understand the building technology, especially mortars, of free standing structures from the Nabatean period (fourth century B.C. to 106 A.D.) and tried to find out the suitable repair materials for the purpose of their preservation. The study was done on two reference monuments, the Temple of Qasr al Bint in Petra, Jordan and the Great Cathedral area in Bosra, Syria.

After the literature review, a damage and condition survey was performed on the reference objects and sampling and on-site testing were conducted. The composition of used mortars, important evidence about the historical working techniques, and mortar preparation techniques were discovered using different investigation methods for material characterisation. The findings concerning the historical mortars and the weathering conditions were the basis for a subsequent definition of necessary preservative actions and for the design of various restoration mortars. A set of probable compatible restoration mortars and "remade" mortars was formulated, tested in the laboratory and by the outdoor walls. The best formulas were applied on-site and finally evaluated. The results achieved within the NAMO project can be used for better planning of how to preserve the valuable relics of Nabatean mortars.

1 Introduction

"*The Archaeometry* (Greek origin), also known as archaeological science, is the application of scientific techniques and methodologies to archaeology. Essential is the interdisciplinary collaboration with mineralogy, geology, material science, prehistoric anthropology, biology and chemistry" (from Wikipedia).

The project NAMO (Nabatean Mortars – Technology and Application) has been carried out under the 5th framework of the INCO-MED program funded by the European Community. The consortium of the project consisted of RSS/BRC from Jordan (Royal Scientific Society – Building Research Centre, Amman), DGAM from Syria (Directorate General of Antiquities and Museums, Damascus), IRCT from the Czech Republic (Institute of Restoration and Conservation, Litomyšl, in 2005 transformed to the Faculty of Art Restoration, University of Pardubice) and ARCS from Austria (Austrian Research Centres Seibersdorf, Seibersdorf) as the project coordinator.

The project deals with the ancient building materials with regard to the mortars of free standing buildings from the Nabatean period in Jordan and Syria. The Nabatean people in the Middle East region are world famous for their rock carved facades in Petra, but the techniques they applied in the making of free-standing structures with regard to the mortars have received little attention.

Various mortars from the Nabatean period have been studied at two reference sites, the Temple of Qasr al Bint in Petra, Jordan and the Great Cathedral area in Bosra, Syria.

A detailed mapping of materials and damages has been carried out at Qasr al Bint to learn about different types of materials and damages, to understand the weathering conditions and the state of preservation. The mapping in Bosra was useless while the remnants of Nabatean mortars can only be found within archaeological probes where the stone material (Basalt) is in very good condition. The mapping operation was accompanied by simple, on-site tests at both reference sites. About 40 small material samples (mostly mortar samples) were taken from each site, which were subsequently studied using various scientific methods to learn more about the composition and the working techniques. The sampling points and the testing locations were registered in the CAD-plans.

Figure 1: Qasr al Bint in Petra, view from the east side

2 Investigation of the Nabatean Mortars

Scientific investigations of historical samples from both reference sites were carried out. The analytical methods employed were x-ray fluorescence (XRF), x-ray diffraction (XRD), differential thermal analyses (DTA/TG), optical and electron microscopy, mercury porosimetry and digital imaging. Additional microchemical tests for testing of the eventual presence of organic admixtures as well as microscopic analysis of paint layers were also performed.

The investigation has discerned four main groups of mortars at Qasr al Bint (for the mineralogical composition, refer to Table 1) [1].

A – renderings of the exterior east facade and from the interior north wall (lime binder)
B – stucco of the exterior east facade (high calcined gypsum and lime binder)
C – joint mortar of the exterior east facade (high calcined gypsum binder)
D – joint mortar of the exterior east facade, of the interior west wall and of the interior cellae (gypsum binder)

Table 1: Qasr al Bint – Mineralogical composition of the major groups of mortar materials and a sample of Petra sandstone in weight percent. Analyses by means of XRD, XRF and DTA-TG. traces (below 1 weight percent)

Mineral	group A: lime plaster & renderings	group B: high calcinated gypsum – lime stucco	group C: high calcinated gypsum – joint mortar	group D: gypsum – joint mortar	Petra sandstone
quartz	71	32	tr	tr	86
calcite	20	23	5	6	tr
dolomite	tr	<5	-	tr	-
kaolinite	5	<5	<5	<5	11
feldspar	tr	-	-	tr	tr
gypsum	tr	24	37	84	-
anhydrite	-	13	54	<5	-

Figure 2: Remnants of stucco decoration at Qasr al Bint

The renderings are characterized by lime binder and predominantly quartz filler from local sands and a minor portion of coarser limestone. They show a layered structure and a quite uniform thickness of 1 to 1.5 cm. The binder-to-aggregate-ratio (B/A – ratio) at the time of preparation was most probably in the range of 1 : 5 (in weight). A particle size distribution of the aggregate obtained by digital imaging on thin sections is given in Table 2.

Table 2: Qasr al Bint renderings – Particle size distribution of the aggregate analysed by digital imaging on thin sections (mean value and standard deviation of seven samples)

mm	percentage of particles smaller than
0,063	0,5 ± 0,1
0,125	6,6 ± 0,8
0,25	37,6 ± 6,1
0,5	78,4 ± 8,8
1	92,7 ± 5,1
2	97,4 ± 4,0
4	100,0 ± 0,0

The binding medium of the stucco of the exterior east facade is a mixture of lime and high calcined gypsum in a ratio of 1 : 1-1.5 at the time of preparation. The main part the aggregate consists of quartz with a minor portion of limestone and dolomite. The mineralogy indicates a B/A – ratio of about 1:2.

Gypsum and anhydrite serve as a binding medium and as an aggregate in both joint mortars of group C and D. Other kinds of filler are negligible; a minor portion of charcoal from the burning process is frequently present.

A fifth, much less well defined group of mortars was found in the lowest parts of the building as a floor screed. They are most probably lime mortars heavily deteriorated and affected by salt crystallization (mostly composed from gypsum). Charcoal up to 4 w-%, potsherds, and brick dust are present as well.

The investigation has revealed four main groups of Nabatean mortars at the Great Cathedral area in Bosra:

A – floor screed: lime mortar very rich in binding medium basaltic aggregate sometimes minor amounts of vegetables and charcoal

B – plaster with vegetable admixture: lime mortar very rich in binding medium with fine grained basaltic aggregate, vegetable admixture (fibers, seeds) but no charcoal, sometimes pumice-like glass

C – plaster with charcoal admixture: lime mortar with a high portion of fine grained basaltic aggregate, charcoal admixture

D – plaster / stucco with coarse limestone admixture: lime mortar with coarse grained limestone aggregate (lower plaster layer), and a high portion of fine grained limestone (upper plaster layer) in addition to basaltic aggregate; no vegetables, no charcoal

3 Weathering conditions and state of conservation

Two reference areas for investigation were defined at Qasr al Bint. One area was selected at the northern part of the exterior east facade starting at a height of about 4 m up to about 10 m. The other one was situated at the interior west wall of the cellar starting from the ground up to about 6 m.

Within both reference areas a detailed mapping campaign and various non-destructive field tests regarding surface moisture, surface salt concentration and water uptake have been performed.

Different damage phenomena on the reference areas were defined and recorded, e.g. flaking, scaling, backweathering, granular disintegration, cracking, outbreaking and loss of joint mortar on the stone masonry, and lacunae, outbreaking and detachment of plaster layers on remnants of renderings, plasters and stucco.

Both the mapping and testing campaign confirmed that rising damp, salt crystallisation and static movements due to earthquakes are the major sources of damage and that the salt load is extremely high in the lower parts of the wall. The highest chlorides concentrations (nitrates also, but in a less clear manner) are accumulated in two zones: firstly in the lowest part of the wall, and, secondly, at the height of approx. 4 m, which corresponds with the border of heavy damages as well as with the border of high surface moisture-values within the interior reference area. The sulphates show a uniform distribution up to the height of about 4 meters.

Heavy damages and deterioration of several sandstone blocks have signalled that progressive corrosion might be the reason for serious structural problems of the object in the future (loss of the load capacity of stone ashlars).

Both the salt concentrations distribution and the state of weathering indicate that rising dampness is the major source for moisture in the lower part of the building [2].

The exterior reference area, which was chosen due to its relics of plaster and stucco, does not exhibit salt damages, despite that the surface concentrations of sulphates, chlorides and nitrates are also very high. This area is above the upper limit of the rising dampness and the source of water-soluble salts most probably originates in dust deposits.

Figure 3: Typical, heavy damages caused by water soluble salts in the lower part of Qasr al Bint masonry

4 Formulas for restoration mortars

Four types of mortars covering the most urgent needs for mortar restoration at Qasr al Bint have been defined according to the damage and condition survey:

- adhesion mortars to stabilise damaged edges of renderings and stucco
- grouting mortars to renew the connection between detached renderings or stucco and the support
- sacrificial plaster to cover parts heavily affected by salt crystallisation
- joint mortar to close the open joints in the masonry.

The overall composition of the *adhesion and joint test mortars* can be summarised as follows:

- Local material sources were used whenever possible except for natural hydraulic lime, which is not available in Jordan or Syria and therefore was imported from Germany.
- The aggregate consists of whitish quartz sand from Petra. The grading curve for the adhesion and the repair mortars is nearly identical to the historical one, which has been identified by digital imaging on thin sections.
- The binding medium was pure lime or low hydraulic materials. To obtain the latter ones the natural hydraulic lime, or a limited admixture of pozzolana, tripoli or portland cement were used. Portland cement was used only to compare several basic properties despite that it was clear from the beginning that such a type of binder is out of the question. Both commercially available lime hydrate and lime putty slaked in pits were employed. Lime putty was very intensively stirred with an electric stirrer before using.
- For the purpose of stucco restoration (remade stucco mortar) a mixture of lime and gypsum was tested. The gypsum was either traditionally burned gypsum from Syria (containing a minor portion of charcoal), or a commercially available one.

Grouting mortars have special demands with regard to workability and application. This is reflected both in the material composition and in the way of testing:

- Liquefiers were admixed to enhance the injection capability in addition to lime or natural hydraulic lime used as the binding medium
- Fine grained aggregate up to 1 mm (mostly only to 0.25 mm) was used to minimise the tendency of setting of the particles prior to the application and to obtain a mortar with a high fluidity and good ability to fill cracks or lacunae.
- Special non-standardized tests were used to describe the properties of the mixtures i.e. an "outflow test" to test the viscosity, a "lacunae test" to test the ability to fill artificial lacunae (this term denotes a cavity between plaster layers or between plaster and support) and an "adhesion test" regarding the bonding capacity of the injection mortar.

Regarding *the sacrificial plaster* the project team decided to test a lime mortar with high porosity and low strength. The sacrificial plaster was formulated as a possibility how to reduce the damages on salt loaded masonry and how to protect the stone from further degradation. The main advantages are the comparably low costs and the easy way of renewal. The various formulas of restoration and remade mortars are given in Table 3.

Table 3: Composition of the mixtures for the laboratory tests in weight percent normalized to 100

Formula No.	PS	JLP	SLP	SG	JG	JT	JC	JP	NHL2	B/A – ratio
2	85	-	-	-	-	-	-	-	15	1 : 5,6
3A	70	23	-	-	-	-	2	5	-	1 : 2,3
3B	67	25	-	-	-	-	-	8	-	1 : 2,0
4A	70	25	-	-	-	3	2	-	-	1 : 2,3
4B	69	25	-	-	-	6	-	-	-	1 : 2,3
4C	75	22	-	-	-	3	-	-	-	1 : 3,0
5A	76	-	19	6	-	-	-	-	-	1 : 3,1
5B	78	16	-	-	6	-	-	-	-	1 : 3,5
6	82	18	-	-	-	-	-	-	-	1 : 4,7
7A	74	26	-	-	-	-	-	-	-	1 : 2,8
7B	76	-	24	-	-	-	-	-	-	1 : 3,1
8	65	35	-	-	-	-	-	-	-	1 : 1,9
9	69	24	-	-	-	-	-	-	7	1 : 2,2
$10A_{1*}$	-	-	-	100	-	-	-	-	-	-
$10A_{2*}$	-	-	-	100	-	-	-	-	-	-

Description of abbreviations:

PS	Petra Sand	JT	Jordanian Tripoli
JLP	Jordanian Lime Putty	JC	Jordanian Cement
SLP	Syrian Lime Putty	JP	Jordanian Puzzolana
SG	Syrian Gypsum	NHL2	Natural Hydraulic Lime**
JG	Jordanian Gypsum		

(*The formulas 10 A_1 and 10 A_2 differ just in the amount of water added, 10 A_2 being the one with less water).
(**The NHL2 employed has been obtained from: Zement- und Kalkwerke Otterbein GmbH, D-36137, Germany, product „Putz- und Mauerfix NHL 2").

Remnants of Nabatean mortars in Bosra can only be found within archaeological probes. Therefore, there was no need for restoration mortar designs, and the formulas to be tested were limited to "remade" historical mortars.

5 Testing METHODS

The various formulas have been tested in three different ways:

- in the laboratory – comprising tests on physical strength, hygric properties and mineralogical and chemical composition
- near Qasr al Bint using an outdoor test wall
- on a very limited scale on the monument itself
- a special test programme has been carried out with regard to the grouting mortars

Mortar specimens with a dimension of 4 × 4 × 16 cm were prepared for the laboratory tests. Special storage conditions had to be applied due to the predominantly lime based nature of the binding medium. They consisted of the storage of the specimen upon a highly permeable fence, of spraying water on the specimen once per week and of weekly turning of the test bodies. Thereby, an all-side carbonization within a reasonable time was ensured.
The laboratory tests were done in the intervals of 28-56-90-180 and 360 days and included the following procedures:

- Tests on the fresh mortar properties prior to the specimen preparation. These were the dropping ball test BS 4551:10, tests on water retention BS 4551:11 and tests on water content and moisture density BS 4551:16 [3].
- Tests on compressive and flexural strength following BS 4551:15 and EN 196 [4] in intervals up to an age of 360 days.
- Tests on water adsorption and saturated or dry bulk density.
- The phenolphthalein test to check the carbonization depth.
- The salt crystallization test partially following EN 12370 [5].

The *test wall* near Qasr al Bint was built in the dimensions of about 1 meter in height to 6 meters in length. It was constructed from stone ashlars of Petra sandstone with the use of a lime-cement-mortar for the base, a lime mortar for most of the wall and gypsum mortar for the uppermost course. Various plasters having a formula similar to the ones for the laboratory tests were applied on the test wall and were evaluated after a period of about 8 and 16 months with regard to salt damages, crack formation and adhesion to the sandstone support.

The most promising formulas were used on a very limited scale at the monument itself during onsite application in March 2005. Three kinds of adhesion mortars were applied within one running meter to stabilize the edges of the damaged plaster on the exterior facade. Two kinds of sacrificial plaster have been applied within an area of about one square meter at the lowest part of the wall heavily affected by salt crystallization on the interior west facade of the cellar.

6 Test results

Laboratory tests:
There were no significant differences in the measured values of the compressive strength and the flexural strength for the various mixtures after 180 days, when nearly all mortars showed a compressive strength between 1 to 2 MPa and a flexural strength between 0.5 to 1 MPa. The only exceptions were the formulas 10 (gypsum binder) giving very high strength values at the very beginning (13 or 19 MPa). Subsequent wetting and drying resulted in a clear tendency towards diminishing the strength (10 or 16 MPa after 180 days).

A water adsorption of 10 to 14 weight percent was determined for all formulas except the ones consisting of gypsum binder (10 A_1 and 10 A_2), which showed a significantly higher values (19 and 16 weight percent). The water uptake of non eroded reddish sandstone from Petra was determined to be 4 to 5 w-% while the eroded sandstone can have a water uptake of up to

14 w-%. Therefore, it can be expected that the new restoration mortars will attract moisture (and salt) to a higher degree than the original stone, which is the preferable situation.

The phenolphthalein test provided evidence about the progressing carbonization of the specimen and indicated that the storage conditions were suitable ones. After 180 days the mortars were carbonized to a very large extent.

The salt crystallization test turned out to be the most significant one to distinguish the various formulas. A gain in weight during the first cycles can be attributed to the crystallization of sodium sulphate within the specimen prior to the disintegration of the fabric. Most of the formulas except the one with gypsum binder survived until the 8th cycle showing a loss in weight in the range between 5 to 10 w-%.

The best results were recognized when employing natural hydraulic lime (formulas 2 and 9) i.e. less than one and 5 % of weight loss after the 8th cycle. Formula 7, though a pure lime mortar, showed comparably good results as well. On the other hand, neither the admixture of cement nor tripoli nor puzzolan resulted in a higher durability. The results of the tests until the 8th cycle are given in the Table 4.

Table 4: Results of the salt crystallization test following EN 12370; negative numbers denoting a gain in weight; n.d. = not determined

Formula No.	weight loss in % of the initial dry weight							
	cycle 1	cycle 2	cycle 3	cycle 4	cycle 5	cycle 6	cycle 7	cycle 8
2	-1	n.d.	n.d.	-2	-2	0	0,1	1
3A	-0,4	n.d.	n.d.	-0,4	3	6	11	11
3B	-1	n.d.	n.d.	-2	1	8	12	18
4A	-0,5	n.d.	n.d.	-1	1	6	9	12
4B	-1	n.d.	n.d.	-1	-1	3	5	7
4C	-1	n.d.	n.d.	-2	-2	2	4	11
5A	-2	n.d.	n.d.	-3	-3	-0,1	6	9
5B	-2	n.d.	n.d.	-3	-3	-1	1	7
6	-1	n.d.	n.d.	-1	-2	0,1	3	7
7A	-1	n.d.	n.d.	-2	-2	-0,2	2	6
7B	-1	n.d.	n.d.	-1	-0,4	3	4	5
8	-1	n.d.	n.d.	0,3	4	6	8	8
9	-1	n.d.	n.d.	-2	-2	-0,5	3	5
10A1	9	11	15	85	disintegration			
10A2	9	11	12	88	disintegration			

The inspection of the test wall near Qasr al Bint took place after the winter period and can be summarized as follows:

- Most of the formulas showed a very low crack density, especially formulas 2 and 9 with natural hydraulic lime as a constituent of the binding medium. On the other hand, Formula 8 being comparably rich in lime binder developed a rather large number of shrinkage cracks.
- A minor amount of cracks within the plasters might be caused due to the setting of the whole structure and not due to mortar shrinkage.
- Each of the test fields has been subdivided into an upper and a lower part by a sandstone „cornice“. Cracks within the plaster are restricted to the upper part presumably due to the following reasons:

- It is very probable that the upper part of the wall dried out more quickly due to seepage of water and a different exposure to the wind. The quicker drying will result in the shrinkage and crack formation at a time when the mortar is still very weak.
- A setting of the whole structure will affect the upper parts to a larger extent than the lower ones.
- Based on the visual on-site inspection and the observations during the sampling it can be stated that the adhesion between plaster and support is very good. Again the best results were found with formula 2.
- The results of the adhesion mortars at the sandstone “cornice” were similar for the various mixtures. All mortars showed a good bond towards the stone and no formation of cracks.

No visible salt damages at the surface of the testing wall have been found after 8 (16) months of exposure; the salt concentration in the sample taken from the height of about 50 cm was in the range of a few hundredth of a percent. Three basic mortar mixtures has been chosen according to the test results as the most suitable for preparation of joint and adhesion mortar (mixtures 4B, 7B and 9; refer to Table 3). These mortars have been subsequently applied on the limited area directly at Qasr al Bint.

A different situation was observed within the tested sacrificial plaster, which was applied to a nearby free-standing block of stone with an apparently high salt load. Significant portions of sodium and chlorine were detected within the mortar (about 0.5 or 1.4 w-%) after eight months and the plaster surface has shown disintegration and flaking in an initial state. Therefore the mortar formula has been changed towards a material richer in binding medium respectively a minor admixture of Jordan tripoli. Two selected mortar mixtures (mixtures 6 and 7B; refer to Table 3) were tested subsequently on the salt-loaded interior wall at Qasr al Bint.

The formulas for the grouting mortars had to be adjusted especially with regard to the particle size distribution of the aggregate. It turned out that fine quartz sand (0/0.25 mm) gave the best results in order to avoid a setting of the mixture prior to the application via a syringe. A commercial liquefier was added to ensure good penetration properties.

Three formulas giving promising results within the laboratory tests (refer to Table 5) have been defined at the end of the testing, with the adhesion comparable to one of the commercially available injection mortars (60 to 100 mN/mm^2).

Table 5: Test series 2 – formulas of injection mortars. Description of abbreviations

Formula No.	W (ml)	PS Red 0,25 (ml) (g)	JLP (ml) (g)	JT (ml) (g)	NHL2 (ml) (g)	Liquidifier (ml)
I_2	70	160 253	75 92	80 58	-	5
I_3	70	160 253	75 92	-	80 56	5
I_4	90	-	75 92	160 117	-	5

W	Water
PS Red 0.25	Petra sand red; fraction smaller than 0.25 mm
JLP	Jordan Lime Putty
JT	Jordan Tripoli
NHL2	Natural Hydraulic Lime
Liquidifier	Melment L10 (Degussa, Germany)

These mixtures were applied once more on the testing wall to fill artificial lacunae (these lacunae were prepared by fixing mortar plates to the test wall in a distance of a few millimetres) as well as to fill "real" lacunae on the limited scale of the reference area of the monument.

7 Summary and conclusions

Regarding the preservation of cultural heritage the whole NAMO project represents an outstanding example of how an ideal restoration project should proceed to formulate the conservation / restoration concept. A step-by-step procedure was chosen starting with the definition of the sources and the extent of damages and with the elaboration of the material characteristics. An extensive amount of data concerning the material properties of Nabatean mortars was generated within the project. Suitable restoration mortars were formulated and analyzed by laboratory and field tests and by an on-site application and evaluated to find the most suitable mortars for conservation purposes.

The project resulted in a much better understanding of the traditional techniques, e.g. the use of high calcinated gypsum at Qasr al Bint, which is a completely new finding, the work steps of stucco making at Qasr al Bint or the elaboration of the material parameters of the hemp fiber lime mortar of Bosra for practical applications. These findings indicate the high level of knowledge of the Nabateans concerning building technologies and materials in the period of their flourishing culture, which are comparable with the other high developed cultures. They knew different kinds of gypsum and lime mortars and they have applied them intentionally having good knowledge about their properties.

With regard to adhesion and joint mortars, it was possible to find new mortars based on simple mixtures with good workability based on the local materials with high compatibility to the historical mortars. The salt crystallization test indicates that the admixture of natural hydraulic lime resulted in the most resistant mortars. The addition of other hydraulic substances like pozzolana, Portland cement, or tripoli did not show a similar effect. Mortars with the natural hydraulic lime have shown very good results at the test wall in terms of workability, crack density and adhesion to the support.

Concerning the grouting mortars, the choice of the aggregates' size turned out to be crucial for the practical application. Several tests with various kinds of aggregates and the employment of different binders and liquefiers have lead to three formulas based mostly on lime binder which will be suitable for a practical application.

The results regarding the sacrificial plaster tested on the salt-loaded surfaces at the Qasr al Bint have demonstrated the ability of the plaster to withstand the crystallisation of the water-soluble salts to some extent. Therefore, they can be regarded as a possible solution to protection from further damage of the stone masonry due to salt attack, but it must be pointed out that the lifetime of the sacrificial plaster is limited and their renewal is necessary.

To sum up, the employment of non- hydraulic or low hydraulic mortars has given promising results in terms of compatibility with the historical materials, weathering resistance, the general appearance (crack formation, adhesion to the support), and the workability on reference areas, which are also applicable to the rest of the monument.

For the Syrian reference site the project generated data which are also of high value for an archaeological interpretation of the site.

With regard to cultural heritage, NAMO has been quite a unique project of cooperation between European and Middle East countries. Most of the cooperation between Jordan and Syria with foreign countries is of an archaeological nature and projects dealing with restoration purposes are to a very large extent missing, although there is great need for it. For the concerned institutions in Jordan and Syria NAMO was a perfect demonstration of the usefulness of a stepwise approach to formulate suitable restoration materials and of the importance of taking traditional materials like lime mortars into account.

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A proposal for test procedure for injection products against rising damp

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Key words: restoration, rising damp, humidity, salts, injection, porous materials, monuments

1 Introduction and content

Humidity in general, and particularly rising damp, is one of the main causes of decay of materials in old buildings and monuments. Due to moisture and salt transport, masonry, consisting of brick, stone, mortar, render, …, as well as wood and paint, are damaged. The decay can have a purely aesthetical to biological (development of fungi and moulds) or physical (delamination and flaking caused by salt crystallisation pressure or frost action) character. But it is usually the moisture that triggers the damage.

Recent masonry should be executed with a mechanical barrier against rising damp. Older masonry usually has no such protection and is regularly subject to rising damp. Rising damp is therefore a main cause of damage in buildings of historical and/or cultural importance.

Masonry suffering from rising damp can be treated efficiently by means of such a mechanical barrier. However, this intervention is expensive, time-consuming and almost impossible in the case of unstable, thick or irregular constructions. Besides it may have serious aesthetical consequences.

The alternative is a physico-chemical barrier by the injection of chemicals which is a cheaper, easier and faster method. Injection products suppress capillary forces by changing the surface tension of porous building materials. They have been widely used in Belgium for decades, with good results. In spite of these positive results, no systematic comparison between the performance of different products has been carried out up till now in Belgium, because of the lack of a simple laboratory test procedure that is sufficiently representative for in practice applications.

Therefore, on demand of both the producers and the official authorities in charge of technical agreements, a test procedure has been proposed by a national working group consisting of contractors, fabricants, a control institution and the laboratories of KIK-IRPA and BBRI, in order to evaluate the efficiency of injection products available on the market as well as new formulations (gels, crèmes).

The test procedure is based on the experience, literature-survey (i.e. [1, 2, 3, 4, 5, 6]) and research [7, 8] of both laboratories. The procedure forms a compromise between the scientific outcome of this research and the literature-survey on the one hand, and practical and financial aspects on the other hand. The goal is a relative simple, fast and cheap, but nevertheless scientifically funded, test procedure that forms the basis for a (Belgian) Technical Agreement (TA), that deals with the initial efficiency of this kind of products.

Identification tests form an essential part of the procedure, since a TA label requires a continuous control of the product composition. The identification procedure is comparable to that used for water repellent agents, which is the determination of the dry weight and analysis by Fourier Transform InfraRed spectroscopy (FT-IR).

The type of substrate is a standardized carbonated mortar sample. The treatment is applied after contamination of the samples with an aqueous solution of a salt mixture (Cl^-, NO_3^-, SO_4^{2-}) at three different saturation degrees (60, 80 and 95 %). The efficiency of the treatment is evaluated by means of capillary absorption tests as well as the determination of the penetration profile of the injection product.

2 Description of the test procedure

2.1 Identification of the product

Four tests are proposed to identify the injection product, which enable the evaluation of the continuity of its quality and composition and to perform conformity-checks on restoration sites:

- determination of the density by means of a pycnometric measurement.
- determination of the viscosity, using a Brookfield Synchro-electric Viscosimeter. If the product is in the form of a gel or a crème, a conus-and-plate apparatus is used.
- determination of the dry weight: 0.5 gram of the product is placed into an aluminium cup. During conditioning at 20 °C and 50% relative humidity (RH), the cup is weighed every 24 hours, with a precision of 0.001 gram. Constant weight is obtained when the difference between two subsequent weighing procedures is less than 0.01 gram. The dry weight of the injection product is expressed as the percentage of the mass of the remaining fraction relative to the initial mass. If no polymerised material is formed during conditioning, the experiment is repeated adding 5 gram of dry mortar powder. This method is identical to the one used by KIK-IRPA and BBRI in their test-methodology for water repellent agents [9].
- analysis of the composition by means of Fourier Transform InfraRed spectroscopy (FT-IR, KBr-method). This method is based on the absorption of infrared radiation in the range between 400-4000 cm^{-1} by the active component(s) and the solvent constituting the injection product. This method is identical to the one used by KIK-IRPA and BBRI in their test-methodology for water repellent agents [9].

2.2 Properties to be investigated

Two main properties of the injection products have to be tested:

- the ability to penetrate sufficiently in a moisture and salt loaded masonry
- the ability to polymerise in humid and salt-loaded conditions resulting in a chemical barrier against rising damp.

2.3 Substrates

Most test procedures described in the literature are performed on wallets. Our initial proposal was also based on this type of efficiency test. For this, the base of a brick masonry wallet is put in contact with a salt solution to simulate the effect of rising damp and salts, and to measure the initial water absorption. After a certain time the injection is performed, and the evolution of the water absorption is evaluated indicative for the efficiency of the treatment against rising damp.

The original program set up included an additional test on single materials to evaluate the penetration properties of the product. For this, the injection product is poured in a hole drilled in samples of brick, stone and mortar. After that, the sample is cut and the treated part is evaluated after wetting the surface.

Because of practical reasons, related to time- and money-issues, this original test procedure was transformed into a simpler and faster set up based on single materials as substrate. This test enables us to perform efficiency tests and migration tests on the same samples. To diminish the costs to be paid by the fabricant, only mortar is considered as substrate in the proposed test procedure. The choice of mortar is based on its sensitivity towards rising damp after treatment. Soon as the mortar is dry, the drying procedure of brick or stone will end up.

In order to obtain a mortar sample that can easily be manipulated, but is also representative of mortars used in older buildings, the following mortar-composition is being used:

- 1 volume part of Portland cement (CEM I, 42.5)
- 1 volume part of hydrated lime
- 6 volume parts of quarry-sand (module of fineness 1.4)

No additives that facilitate to demould the mortar samples (size: 4 × 8 × 16 cm³) are used.

After hardening, a hole (diameter: 2 cm ; depth: 6 cm) is drilled in the middle of the mortar sample (figure 1). The samples are placed in a CO_2-rich atmosphere till complete carbonisation. The carbonisation is checked using a phenolphthalein-indicator on a sample cut in the middle.

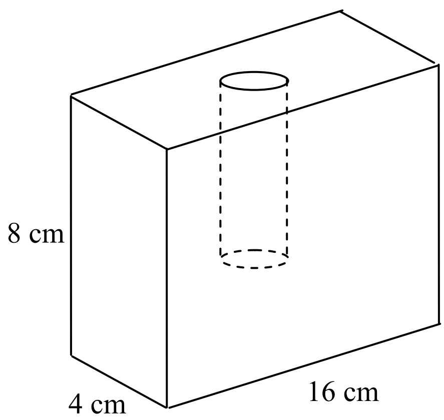

Figure 1: shape and dimensions of the test samples

2.4 Characteristics of the samples

Every sample is subject to a capillary rise test according to the conditions described in EN 1925. The largest surface (8 × 16 cm²) is the absorption surface. The moisture uptake after 2 weeks is considered as the saturation moisture content (m_{0s}).

2.5 Preparation of the samples

The set up of the test procedure is as follows:

- The samples are dried at 45±5 °C till constant weight (mass difference between two subsequent mass-determinations, with an interval of 245 hours, is less than 0.1 %).
- Pre-conditioning of a salt-solution, containing 0.5 mass% of NaCl, 0.5 mass% of KNO_3 and 2 mass% of Na_2SO_4. The samples are contaminated with this salt solution as to obtain a saturation degree of 60±5, 80±5 and 95±5%.
- Each sample is packed individually in a watertight container during one week (20±3 °C) to enable the homogeneous spreading of the salt solution.
- After control of the saturation degree (by weighing the samples), the injection product is poured in the drilled hole. The amount of product is 1/4th of the prescribed amount (also

in the case of products formulated as a gel or crème). In case no consumptions are recommended in the technical sheet, 16 ml of product is applied. By doing so, it will be easier to make a distinction between excellent and mediocre or insufficient performing injection products.

- The drilled hole is closed to prevent the possible evaporation of volatile active compounds (such as silanes) and to render the outside of the sample water repellent.
- Each sample is placed individually back in its watertight container for 28 days (20±3 °C).

2.6 Efficiency test

The sample is submitted to a second capillary rise experiment according to the test conditions in EN 1925 (in an open atmosphere, enabling capillary water to evaporate), without drying previously. The absorption surface is again the surface of 8 × 16 cm². These test conditions simulate on site situations where injection products are to be injected in moisture and salt loaded masonry. Moreover, products for which these conditions are not favourable for polymerisation of the active compounds can be recognised. The experiment continues till constant weight of the sample (m).

After that, the following operations are carried out:

- drying of the sample at 45±5 °C (m_d) till constant weight
- conditioning of the sample at 20±3 °C and 95 RH until constant weight. This enables the determination of the hygroscopic moisture content (m_h)

The capillary water uptake (m_c) is calculated according to the formula:

$$m_c = m - (m_d + m_h)$$

The amount of capillary moisture uptake is a measure for the efficiency of the treatment that reflects the quality of the product and may be expressed as (for each of the tree samples; being initially saturated to 60, 80 or 95%):

$$\text{Efficiency (\%)} = 100 \times (1 - m_c/m_{0s})$$

This efficiency or quality criterion is related to the performance of the product applied in conditions representing on site situations and might be not valid in case the product is applied in a dry and salt-free medium.

2.7 Ability of the product to migrate into the material

To determine the migration properties of the injection product, the samples are cut into two. The sawn surface is parallel to the surface of 8 × 16 cm². Subsequently:

- drying of the sample at 45±5 °C till constant weight
- spraying of water on the sawn surface. The non-absorbing part of the surface is considered to be treated.

The ability of the product to migrate in a (wet) material is expressed as the non-absorbing and hence water repellent surface, relative to the total surface of the sample. As is the case for the efficiency, the migration properties are influenced by initial moisture content (60, 80 or 95% of saturation water-content).

3 Conclusion

Rising damp is a moisture source mainly occurring in monumental constructions, since recent buildings are supposed to be constructed in such a way that they do not suffer from this phenomenon. According to the BBRI-statistics [8], about 1/3rd of all construction problems are directly related to humidity, and about half of the renovation interventions are linked to rising damp and hygroscopic salts [10]. These figures indicate the importance of the treatment of rising damp on the Belgian level. According to the international bibliography, the importance of this phenomenon on European and international level is within the same range.

Mainly because of financial reasons, this procedure, in which single substrates are used, has been developed on a simpler and more practical way compared to our initial proposal. The set up is based on the experience of both laboratories. The test conditions are chosen as to be representative for practice situations of rising damp. Therefore, it is expected that results obtained from this test procedure can be related to the in situ performance of injection products against rising damp.

At this moment, the above proposed test program is running for the first time. Hence, experimental results obtained within this procedure will be available shortly. Some well-known commercial products, with which we have a large laboratory as well as on site experience (both excellent and insufficient performing products), are included. Hence, they serve as reference injection products to validate the test procedure.

We are well aware of the fact that excellent products might not perform perfectly in this procedure. This is mainly due to the fact that only one quarter of the normal product quantities is applied to the samples, and that the samples are larger than the normal distance between two drilled holes in a wall that has to be injected (which usually ranges from 10 to 12 cm). Anyway, because of these severe test conditions, it will be possible to make an objective distinction between excellent and mediocre or insufficient performing products.

Such a standard procedure may stimulate the producers to develop new and more effective injection products, and to let them test on a scientific and systematic base. This will enable the end-users to make a better comparison between products, and to dispose of even better products in the near future.

The innovative properties of this procedure lie in its rapid and small-scale character. If it turns out that this procedure gives results that reflect the performance of products applied on site, this procedure might be proposed on the European level (i.e. CEN/TC 346 “Conservation of cultural property”) as a standard test methodology.

As so many test procedures, also this procedure is subject to changes in scientific knowledge, experience and new developments in product types. Since this is a very new procedure, it evidently is open to suggestions from other experts. A very important topic for this kind of products is the testing of durability aspects, that we hope to investigate shortly.

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Assessing compatibility in conservation of masonry structures on archaeological sites

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Key words: compatibility assessment; masonry conservation; incompatibility index; decision support system

1 Introduction

The conservation of the Mediterranean and European heritage is strategic for the Community because this is an important component of our identity. In spite of the awareness that people have been paying to it, this patrimony has been progressively reduced over time, due to environmental conditions and bad interventions, where incompatible actions and policies are not uncommon; on the contrary, it is a fact of the daily experience that careless interventions are frequently found worldwide.

The PRODOMEA project comes within the framework of the INCO Programme with the intention of developing the theme of compatibility of conservation actions on archaeological masonry and opening this concept not only to strictly physical parameters but also to operational and local context considerations.

PRODOMEA project faced a problem that, although in different environmental conditions, is common to all the Mediterranean Basin. In the field of conservation the concept of 'Compatibility' is particularly relevant, but most archaeological sites suffer from wrong intervention actions, practices and policy decisions and many cultural elements have been definitively lost due to these wrong interventions. To support the research the project team has chosen 5 archaeological sites in the Mediterranean Area as case-studies: (Giannutri (I), Troia (P), Mekawer and Petra (J), Damascus (Syr). To study these actions through several sampling campaigns and tests was the first objective of the project. Updated analytical methodologies were applied in order to characterize both the archaeological materials and the past conservation actions, as well as to describe the environmental effects acting on them. The objective was to learn from past interventions and to find therein a springboard for better methods and more appropriate approaches.

It is evident that there is an increasing awareness of the need to follow high quality standards in conservation actions and there is an increasing acceptance of the inclusion of scientific knowledge in management and planning activities. The PRODOMEA Compatibility Approach, having understood this situation, aimed at providing management instruments for all the actors of the conservation process, and has settled the compatibility model as its core concept and the Incompatibility Degree, the Knowledge Base and the Decision Support System as its major operative tools.

In order to do this, it was necessary to build up a friendlier and structured methodology for finding sustainable conservation strategies that might be alternatives to the approaches that are based on scattered data and mostly supported in unstructured and not validated concepts. The result has been the definition of a new approach for the assessment of compatibility of conservation treatments and its transformation into a useful IT tool in order to better exchange and manage the knowledge on compatibility and conservation treatments.

The project took advantage of the studies carried out in the last few years on the Compatibility and Conservation concepts, and considers it has significantly improved in originality, degree of innovation and progress beyond the state of the art. In particular:

- The PRODOMEA approach considers Compatibility not only in its strictly physical parameters but also in what concerns the operational, environmental, social and cultural compatibility criteria;
- This approach has been designed to become a "guiding instrument" applicable to masonry conservation to support technical management and to implement more effective and sustainable interventions, focusing the assessment on a "compatibility tree" that leads to the quantification of the "Incompatibility level" of any given intervention. The use of quantifiable indicators for defining the Incompatibility level constitutes a real innovative methodology in Cultural Heritage.

2 Assessing compatibility: the PRODOMEA compatibility approach

Compatibility is a widely used concept in conservation. It is used either as a generic or as a strict concept, but a proper definition is lacking and a clear understanding of how to interact with it in practical terms is not available so far. Principles of conservation of cultural heritage, in which compatibility can be included, can provide a framework of options that make an action acceptable or unacceptable, but they cannot be considered as having a universal value and they provide just vague indications of operative value. The validity and boundaries of those principles may vary according to the contexts in which one will have to operate, being of a historical, cultural, social and environmental nature, and the fact of having a cultural nature means that it is not straightforward how to turn them into concrete decisions for operative purposes.

It is not easy to find a simple and generic definition of the term compatibility and the consulted literature reflects this difficulty. Quoting from documents published elsewhere, 'in spite of the fact that each one might have an idea of what are "proper and compatible" materials, it is felt that there is a need for a better definition of these concepts when historical structures are concerned, although bearing in mind that "absolute compatibility" is more a wishful thinking than an objective and feasible reality' [1].

Applying the concept to the overall performance of any given intervention or treatment, the EU-POINTING project team adopted the following definition: "an intervention or a treatment shall not cause any damage (technical or aesthetical) to the historic material. The intervention or the new material must be as durable as possible" [2].

The building up of a road towards a Compatibility approach in Heritage Conservation for masonry conservation required the exploration of many issues and it had to include the development of proper methodologies and tools to assess how close or distant each action is to full compatibility. The Compatibility Approach provides support for selecting appropriate methodologies (strategies) and tools (tasks) to introduce compatibility in the conservation process and to assess the incompatibility level as part of an integrated conservation planning for masonry conservation.

When addressing the concept of Compatibility and its meaning, the team assumed that, in general, conservation interventions, namely in archaeological sites, carry a certain level of risk and that it is neither technically nor economically feasible to advise that only interventions without risk should be acceptable. Therefore, the ultimate achievable aim is certainly not to find "perfectly compatible" actions, but to find those that minimise the degree of incompatibility. The Compatibility Approach of the project has been designed to become a "guiding instrument" for masonry conservation with a relevant supporting role in technical management, aiming at having more effective and sustainable conservation interventions.

The underlying idea on which the approach is based takes as its criteria the technical, operational, environmental, social and cultural components of compatibility. These criteria were integrated into a coherent framework and a logic reasoning flow chart in order to facilitate the integration of multiple and diversified components in the assessment of compatibility in order that it might be used as an operative tool in the conservation process.

This framework is a tool for ordering and organizing knowledge and consists in considering the conservation process in its full extent and the compatibility concept in its entire complexity and in further adopting a rational subdivision for both concepts. The logic reasoning guides the user from the higher level of complexity to the workable basic components and from the quantification of these lowest level components up to the assessment of the full operation.

The final performance of a given conservation intervention is influenced by a large set of factors, components and constraints, and this statement is valid whether we consider them or we simply ignore them. That set of factors can be grouped in a "compatibility tree" where the major branches are the physical content, the environment factors, the operational background and the socio-cultural context, branches that are subsequently subdivided into secondary levels, the basic components designated as "compatibility indicators".

Briefly, the first order branches can be defined as follows:

i) the *physical content* represents the characteristics of the materials and includes the intrinsic properties responsible for the effective performance of the intervention action, considered in its material side;

ii) the operational background includes all the possible factors of an immaterial nature (availability of tools, practices and constraints) that influence the quality of the conservation intervention through their interference in the decision makers, planners and operators;

iii) the *socio-cultural* context includes all the social components associated to any conservation intervention that, although having no direct impact on the material incompatibility, are relevant for facilitating the acceptation of the conservation intervention by the local communities and may play a significant role in the final quality of the intervention;

iv) considering that the interaction between the conservation materials and the masonry materials depends on the external factors, an assessment of the *environmental* constraints is also considered.

The major challenge in the assessment of compatibility is to be able to define a precise methodology to integrate the information that is provided by each individual Compatibility Indicator (CI) and to prepare the way to reach a quantified value for the Degree of Incompatibility. In this approach, the Compatibility Indicators (CIs) are the basic factors of Incompatibility and are assumed to be quantifiable in terms of their potential influence in the overall incompatibility. Any CI is supposed to contain relevant information, but inevitably each one, individually, is only a partial component of the overall explanation. Each CI has a role in the final performance and in principle it can be assumed that it is possible to rate its importance according to the relative role that it plays in terms of Incompatibility.

In order to make it possible to work with this non-uniform reality it was necessary to create a system of translating the diverse terms (quantifiable or descriptive) into a uniform system that would allow the integration of components that *per se* constitute an intrinsically inhomogeneous set. This system consists of attributing a position in a rational graduation between 0 and 10 to each Compatibility Indicator, according to its potential as inducer of negative (harmful) effects for the conservation objectives. In other terms, the rating given to each CI indicates how its expected action is positioned in terms of higher or lower degrees of incompatibility potential.

The project has advanced with a certain number of rules for the rating process as a first approach to the problem, finding support in personal research data or in the available literature, but most of them are just based on logical and comparative reasoning. This means that further research is required to validate and calibrate the system in order to properly build up a reliable and strongly supported methodology.

The rating system was conceived and defined with the expectancy that it will be possible to integrate the identified indicators in a quantifiable unified assessment. This quantifiable assessment was translated into a generic concept called Incompatibility Degree, which fits well with the physical-chemical criteria and which assumes slightly different designations when the other groups of criteria are concerned, specifically, Operational Incompatibility, Socio-Cultural Mismatch and Environmental Constraints.

Once the indicators are identified and the rating value attributed, it is possible to compute the Incompatibility Degree by means of an appropriate mathematical formula [3]. The obtained indexes for the different criteria are numbers that help to understand the overall compatibility of a given conservation operation or to assess the local (specific) incompatibility of a given conservation treatment. As indicated later, the approach was also conceived for working as a checklist for finding the less harmful alternatives of any given conservation action and it was further deployed as a design tool applicable to new interventions.

In order to illustrate how the methodology works, two tables applicable to the assessment of Past Interventions are included herewith. Table 1 shows the most common combinations of "substrates" and "conservation materials" that can be found in archaeological sites. Table 2 shows the physical-chemical indicators and the respective ratings for a typical conservation treatment. This table illustrates a situation where indicators can be measured and ratings can be given with experimental support and be scientifically justified. On the other hand, other tables contain the Indicators and ratings, for example, for the operational branch of compatibility, aiming at illustrating the application of the system to typically qualitative indicators. It tries to evaluate the quality of operative choices – that qualify the conservation process – taken by the decision-makers and planners at the time of the intervention.

Table 1: Common combinations of "materials" and "substrates" in archaeological sites

			Conservation materials			
			Mortars	Consolidants	Water repellents	Groutings
			1	2	3	4
Archeological materials	Traditional masonry	A	A1	-	-	A4
	Stone	B	B1	B2	B3	-
	Ceramics	C	C1	C2	C3	-
	Plasters and renders	D	D1	D2	D3	D4

This theoretical background is the support for the definition and building up of a Decision Support System that will constitute an important IT Tool at the service of the conservation practitioners.

3 Assessing compatibility: the PRODOMEA DSS

When analysing the Compatibility concept and when trying to extract conclusions as to its application to real situations, one immediately realises that the variables involved are multiple and diverse and that applications of the concept in practical cases so far are scarce or nil. In spite of the difficulties that can be anticipated, we consider that the methodology presented above can help to overcome these difficulties. Therefore we tried to build up a procedure to help the actors in the conservation field to deal with incompatibility and to install reasoning procedures that minimise the risk of adopting solutions that could lead to incompatible performances. The idea is not to answer "what is the solution to my problem?" but to support the decision process where "the solution" will show up as a consequence of a more complete and structured reasoning sequence. In fact we cannot expect that this approach will lead straight to the "single best answer", which is why we cannot name it as an expert system but rather as a Decision Support System.

Table 2: Incompatibility risks for combination A1: repair mortars for traditional masonry

Criteria	Compatibility indicators	Incompatibility risks (rating scale)*
Chemical and mineralogical composition	Type of binders (S&R)**	Similar → 0 Different → 10
	Type of aggregate (S&R)	Similar → 0 Different → 5
Pore space	Porosity (S&R)	[0. 9 Ns < Nr < 1.1 Ns] → 0 [0.7 Ns < Nr < 0.9 Ns] → 5 [Nr < 0.7 Ns] → 10
Visual properties	Total colour difference (ΔE*) (S&R)	Lower than 3 → 0 Between 3 and 5 → 5 Higher than 5 → 10
Thermal properties	Thermal expansion coefficient (ε) (S&R)	[0.9 $\varepsilon_s \leq \varepsilon_r \leq$ 1.1 εs] → 0 [1.1 $\varepsilon_s \leq \varepsilon_r \leq 1.5\ \varepsilon_s$] → 5 [$\varepsilon_r \geq 1.5\ \varepsilon_s$] → 10
Mechanical properties	Bending strength Compressive strength Modulus of elasticity (S&R)	Values different by less than 10% → 0 Values between 10 and 50% higher → 5 Values higher than 50% → 10
Hydrophilic behaviour	Water absorption coefficient Water vapour permeability Drying index (S&R)	Values different by less than 10% → 0 Values between 10 and 50% higher → 5 Values higher than 50% → 10
Presence of salts	Salt content (S)	Free of salts → 0 Sparse presence of salts → 5 Heavily loaded with salts → 10

* The ratings are typified for 0, 5 and 10 as references for low, medium and high risks, although admitting that any value between 0 and 10 can be applied.
** S stands for substrate; R stands for repair mortar used in the past interventions

The compatibility approach briefly presented was transplanted into an informatics algorithm that constitutes a DSS – decision support system. This IT tool applies the new approach for the assessment of the level of incompatibility of conservation treatments on masonry architectural assets and was designed to answer two main questions: i) am I able to assess the degree of incompatibility of past conservation actions? ii) how can we identify and select the most appropriate actions for a more compatible new intervention?

The PRODOMEA IT tool can be reached on the internet at PRODOMEA web site (www.PRODOMEA.com) and allows you to use the IT Tool in several ways:

Knowledge Base (KB): it contains the different groups of documentation that constitutes the knowledge base of the PRODOMEA project, above all about Compatibility and Conservation of archaeological mortars. The main section of KB is dedicated to Materials and Techniques. It constitutes the knowledge base with which the DSS interacts when applying the compatibility evaluation procedure. It contains, as basic reference data, the data coming from the case-study sites of the PRODOMEA project. Literature is another section of KB. It constitutes a sort of digital library that was not created as a real database, but that can be seen as an archive, subdivided into thematic categories where it is possible to find interesting and detailed documentation about new methods of testing or experimental conservation procedures studied inside the PRODOMEA project or in other European projects. Finally, the DSS short reports are a sort of "box" where a part of the results of full application of the DSS are, dynamically, stored with all the PRODOMEA case-studies.

Case-studies: include the presentation of the conservation actions that were analysed and evaluated from the Compatibility point of view on the PRODOMEA archaeological sites. It allows us to study the past treatments, as well as some new interventions, and analyses their 'incompatibility rating' in order to identify and describe several case studies of masonry treatment that can be seen as "best or bad practice", also in terms of technologies and materials, but also from the point of view of sustainability.

DSS – PRODOMEA decision support system: this is a tool to apply the new PRODOMEA approach for the assessment of the level of incompatibility of conservation treatments on masonry architectural assets present in archaeological sites. The PRODOMEA-DSS aims at being a helpful instrument for:

- evaluating the Incompatibility Degree of past interventions. Incompatibility assessment in past interventions is the procedure that scientists, conservators and restorers could use to evaluate the past interventions. This procedure can be applied as a "control tool" in order to identify and evaluate best and bad practice,
- choosing the less incompatible intervention processes, or the best intervention concept, or the more appropriate actions in new interventions. This part of DSS is structured as a procedure aiming at helping the different key-actors of the conservation process to understand where they can encounter problems linked to Compatibility when preparing their conservation plan, when defining the conservation concept or when designing the conservation actions. The PRODOMEA team has identified 8 key-phases, each of them containing a list of recommended actions and a check-list.

a) Assessing past interventions

The unsatisfactory effect of past conservation treatments can be caused by several aspects that occur during the conservation intervention, for example: misfit of the conservation concept; application of non compatible / non suitable treatments; misinterpretation of the environmental stresses & factors; lack of skills of the operators; bad selection of contractor; lack of control during the intervention. For the assessment of past interventions the DSS includes two levels of assessment, referring to the two typical main phases of the conservation process:

- the upper level of the conservation process refers to the conservation concept aiming at comparing its conceptual visions with the general wide context of its practical application. The parameters involved are those referred to as the Operational Background and Socio-Cultural Context. They measure the interactions of the planned actions with the surrounding context and take into account the relationships between them;
- the technological level of the conservation intervention, in which the assessment refers mainly to the physical and technical characteristics of the materials, the environmental constraints and the operational parameters strictly linked to the chosen conservation technologies.

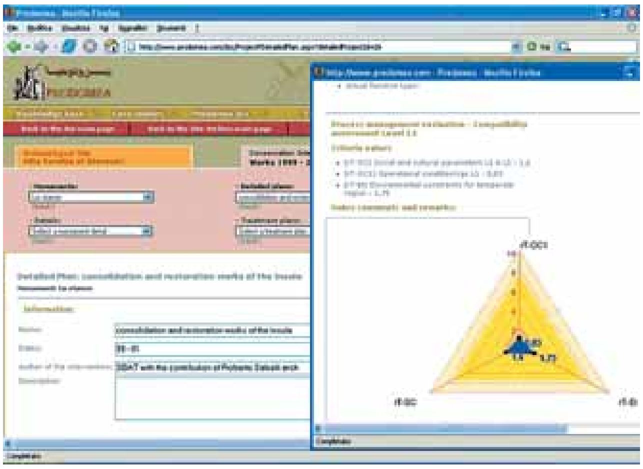

Figure 1: The assessment of intervention of 1999 in Giannutri

b) Choosing the less Incompatible intervention processes

The new Intervention DSS is structured as a procedure aiming at helping the key-actors to understand where they can encounter problems linked to Incompatibility when preparing their conservation plan, when defining the conservation concept or when designing the conservation actions. We could identify 8 key-steps, each of them containing a list of recommended actions that, in the experience of the PRODOMEA team, are fundamental for the remedy of masonry damage and for reaching a high compatible and sustainable level in the conservation of the concerned monument.

The IT Tool procedure provides:

- a check list for the preparation of each intervention step that the key-actors could follow in order to prepare a 'more qualified' conservation plan,
- sub-routines for the evaluation of the level of Incompatibility of some activities that the key-actors are planning, giving them the idea of 'how (in)compatible' is the action that they are undertaking. Or rather, what kind of problems they will eventually come across.

The inclusion of this kind of 'sub-routines' for the evaluation of the Incompatibility Degree of the actions previewed in each phase may certainly be an interesting use of the system. In this scenario, the system can be seen as a "design tool" to support end-users in defining the less Incompatible conservation plan or conservation actions.

The PRODOMEA 8 key-steps:

- STEP A – Pre-diagnostic phase – This phase includes a component of investigation that, in medical terms, corresponds to what is normally called anamnesis and it includes a first survey of the degradation forms and of the distinctive materials. The aim of this step is to identify the monument, its history and architectural significance and to have a first picture of its state of damage, in order to be able to correctly address the following phases of diagnosis and intervention.
- STEP B – Diagnostic phase (or Diagnosis) – The main aims of the diagnosis are the identification of the causes of damage of the decay processes active on site and the preparation for the selection of solutions for the identified problems. In order to achieve these aims, on site and lab studies may be required, namely for the characterisation of materials and decay products, for the quantification of decay rates and for the interpretation of the masonry and mortar damage processes.
- STEP C – Conservation concept – The main aim of this phase is the construction of a theoretical and ethical framework within which the practical conservation actions

should be selected and deployed. It should include a precise identification of what is to be conserved, the indication of the major conservation actions needed, the identification of the acceptable procedures (and of the non-acceptable, if critical) and the limits of the intervention. The goal of this step is to provide a basic framework of information which is necessary to determine if the conservation intervention should be initiated and how to monitor the subsequent implementation phase.

- STEP D – Intervention actions – This step uses the information provided by the diagnostic phase and, on the basis of the decision taken in the Conservation Concept phase, it provides the scientific and technological background for the definition of compatible conservation measures. The overall aim of the phase is the preparation of a complete framework that will contain the basic information to be transmitted to the conservation-restoration team concerning the execution of the conservation actions.
- STEP E – Intervention plan – It aims at building up an efficacious tool for arranging the intervention "working chains" and to check the consequentiality and mutual implications of all intervention phases, from the project desk to the work site. Of particular relevance are the precise identification and scaling of the intervention actions, the establishment of minimum requirements for the operational team, the estimation of costs and the anticipation of the critical issues that might reasonably be expected.
- STEP F – Selection of operators – The selection of operators is the turning point from the research and planning steps to the execution and implementation phase. A bad or improper selection may jeopardise an entire process, even those that have fulfilled the previous phases at high standards. The selection shall address the team composition (academic background, practical experience and distribution of responsibilities) as well as the comprehensiveness of the work proposal, the work phasing and also the possible restrictions or modifications raised or suggested by the applicants about the tender work programme.

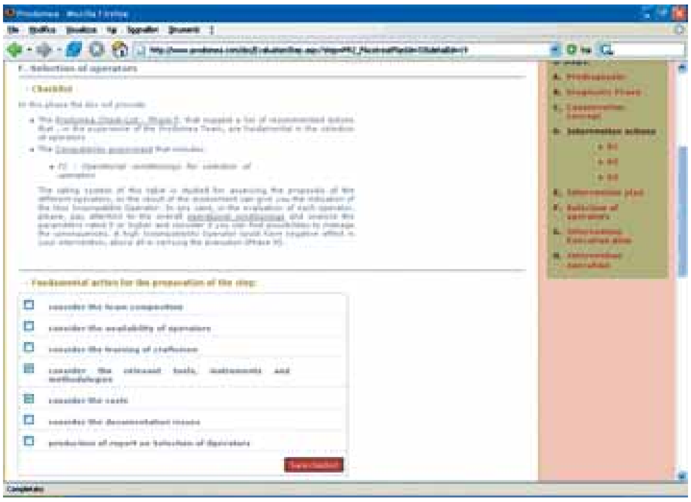

Figure 2: New intervention procedure: the check-list of Step F

- STEP G – Intervention execution plan – The executive phase in a restoration intervention is a decisive step, since any mistakes made in this phase may jeopardise all the good intentions, plans and studies carried out in the preceding phases. In this context, the contractor, as a key-player of this step, shall define precise methodologies for the different types of tasks to be carried out and shall submit them for the appreciation and approval of the person responsible / designer of the intervention.
- STEP H – Intervention Execution – Intervention Control – A good or bad result is "materialised" in this phase, when operators have the "hands on" with all the

consequences that can be easily anticipated. The operators and supervisors must respect the plans and directives, as well as taking into account that even the best plan may undergo improvements. The operators must show high availability to interact with the site responsible, namely whenever any modification or improvement is considered possible or desirable. The site responsible must deploy a strict supervising scheme with permanent control over the technical and logistic aspects of the works and should never delegate to the contractor the ultimate capacity to decide on any relevant modification to the work plan. The contractor must report on all the actions carried out, the materials used, the procedures adopted and the final condition of the object achieved with the intervention works. It is also expected that the contractor complement the condition survey maps with the information gathered during the intervention works.

c) Applying the Compatibility approach

The progress made by the PRODOMEA project in terms of the Compatibility concept leads to the conclusions that no specific technology per se, in absolute terms, should be given a quality of “compatible”. In other words, when attributing a numeric rating of incompatibility to each combination of ‘material’ in ‘socio-cultural context’ with ‘operational conditionings’ and under given ‘environmental constraints’ conditions, we are implicitly assuming that universally ideally compatible interventions do not exist.

However, the PRODOMEA project has studied and assessed a very significant number of conservation technologies and archaeological materials, whose descriptions and characterization are a very important component of the project outcome.

The cultural context and the operational conditionings have relevant influence on the overall compatibility of a given conservation action and they should not be considered as irrelevant. However disregarding these immaterial components may bring about very negative consequences. They may include political and administrative reasons and both can be the cause of inappropriate conservation practice. The sudden availability of some amount of money to be applied to a specific monument may “oblige” the site manager to proceed rapidly to the intervention phase with insufficient diagnosis and even lack of information about critical aspects. The consequences of such procedure may be very detrimental to the adequate preservation of the monument.

Similar consequences may result from the application of administrative rules that were not specifically drawn up with the activity of monument conservation in mind. Simple questions such as the accreditation of operators (for instance by requiring a too high economic background for the registering process) and the selection procedures (for instance by giving the cost an excessive weight in the selection process) may completely jeopardise an entire conservation intervention. The precise definition of the conservation objectives to be reached, the requirement of well-prepared conservation teams (with demonstrated results and with obligation to engage the persons indicated in the tender documents in the site) as well as the attribution of the highest weight to the technical quality of the proposal are the antidotes at reach when such drawbacks are identified and wished to be overcome.

Automatic and uncritical adoption of foreign ‘compatible’ technologies is risky and should be avoided. When going through the PRODOMEA supporting documents it is easily seen that the local conditions play a decisive role in the Incompatibility Degree and therefore it is obvious that any technology has to be screened in the light of the local conditions before being adopted. The critical assessment provided by the PRODOMEA approach is considered as a relevant instrument for proper adaptation of such technologies.

4 Conclusions

The mid-term review underlined how “ambitious” the project was but the results testify that the goal was reached, either in the terms of the innovative approach that had been drawn up, identifying methods and procedures for integrating compatibility and sustainability concepts with the sector of the conservation of archaeological heritage, as well as in its transformation into a useful IT tool. Furthermore, the introduction of Compatibility Indicators and the related assessment tool was a pioneer action in the conservation of cultural heritage.

Although it is evident that there is an increasing awareness of the need to follow high quality standards in conservation actions and there is an increasing acceptance of the inclusion of scientific knowledge in management and planning activities, the experience of these 3 years of research tells us that a quantifiable evaluation method of the level of Compatibility is not easy to accept. So the route towards a compatibility approach may be long and passes through the integration of new attitudes and the exploration of methods and tools that might be instrumental in carrying out compatibility assessments. But it will require the support of operative instruments, like PRODOMEA tools, in order that this approach might be introduced as a normal component of the conservation process: assessing the incompatibility potential, or risks, as part of an integrated conservation planning.

The challenge for the future may be the possibility to test the Compatibility Approach and its impacts more widely, and to extend this approach not only to the conservation of archaeological masonry but also to try to find a method to assess the restoration actions, providing management instruments for all the actors of the conservation process.
In the future we have to be able to offer approaches, like PRODOMEA:

- that are flexible conservation management procedures, necessary to successfully find an action that minimises the degree of incompatibility,
- that will use the opportunities given by information technologies and aim at becoming a practical instrument in conservation practice to be used everywhere.

5 Acknowledgements

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Effects of the weathering on stone materials: assessment of their mechanical durability

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Key words: stones, durability, artificial ageing, ultrasonic pulse velocity, drilling resistance, image analysis

1 Objectives

To achieve the objective of realising a reliable stone material qualification procedure for the short, medium and long term we need affordable measures and methodologies able to reach general consensus to draft standard methods for evaluate the “Stone Durability” in natural stone market.

The objective of the project, as requested by the CENT TC 246, was the development of appropriate and innovative methodologies based on laboratory and “in situ” testing procedures and modelling techniques for the evaluation of stone durability taking into account its mechanical properties [1] and adopting portable NDT/MDT techniques [2].

2 Methodology

2.1 Selection of rock categories

Due to the vast variety of lithotypes present in the European Natural Stones Market the project team, for studying the stone durability, decided to limit the types of stone materials to be tested to a list of most representative Rock Categories (RC, high strength igneous rocks such as granite, diorite etc. were not considered in this project since their durability limit is, in general, higher):

- *Marble* with two types of fabric = *homeoblastic* and *heteroblastic.*
- Limestone with two grain sizes = fine grained and coarse grained.
- *Sandstone* which exhibits transverse anisotropy (i.e. one plane of isotropy) = *parallel* and *perpendicula.*

2.2 Selection of monumental test sites

The stone durability was verified both with respect to accelerated ageing tests and to natural weathering in different exposure site in the north, central and south European climate. In order to try to correlate the accelerated cycles to the real time the natural exposure sites have been selected in such a way to be present close to Monumental Buildings, having one of the selected RC.

For this reason the quarry source and the type of RCs have been selected after having chosen an easily accessible monument:

- *Marble homeoblastic* and *heteroblastic* = S. Maria del Fiore Cathedral (Florence, IT).
- *Fine grained limestone* = St. Paul Cathedral (London, UK).
- *Coarse grained limestone* = Politecnico di Torino (Turin, IT).
- *Sandstone parallel and perpendicular* = Birkenfield Monastery (Bamberg, D).

2.3 Selection of source Quarries

The quarries from which the testing stone specimens were got are the same quarries from which the stones present on the selected monuments originated, that is:

- *Gioia Quarry, Carrara (IT)* for the homeoblastic marble.
- Cervaiole Buca Quarry, Camaiore (IT) for the heteroblastic marble.
- Portland withbed Albion Quarry, Portland (UK) for the fine grained limestone.
- Vicenza Arcari Quarry, Vicenza (IT) for the coarse grained limestone.
- Sander Schilfsandsteinbruch “Hermannsberg”, Hassberge, (D) for the anisotropic sandstone.

2.4 Specimen preparation

At each quarry a large oriented block has been selected and the amount of specimens needed for the AA and NA tests have been properly obtained. Every small specimen with 100 × 50 × 50 mm size was cut maintaining the original orientation as in the block (cut angle in Fig. 1).

The RCs tested have been:

- *MG (*the homeoblastic marble from Gioia Quarry, Carrara, IT).
- *MC* (the heteroblastic marble from Cervaiole Buca Quarry, Camaiore, IT).
- *PW* (the fine grained limestone from Portland withbed Quarry, Portland, UK).
- *VA* (the coarse grained limestone from Vicenza Arcari Quarry, Vicenza, IT).
- *SC* (the anisotropic sandstone cut in the contro direction).
- *SV* (the anisotropic sandstone cut in the verso direction) from Sander Schilfsandsteinbruch “Hermannsberg” quarry , Hassberge, D).

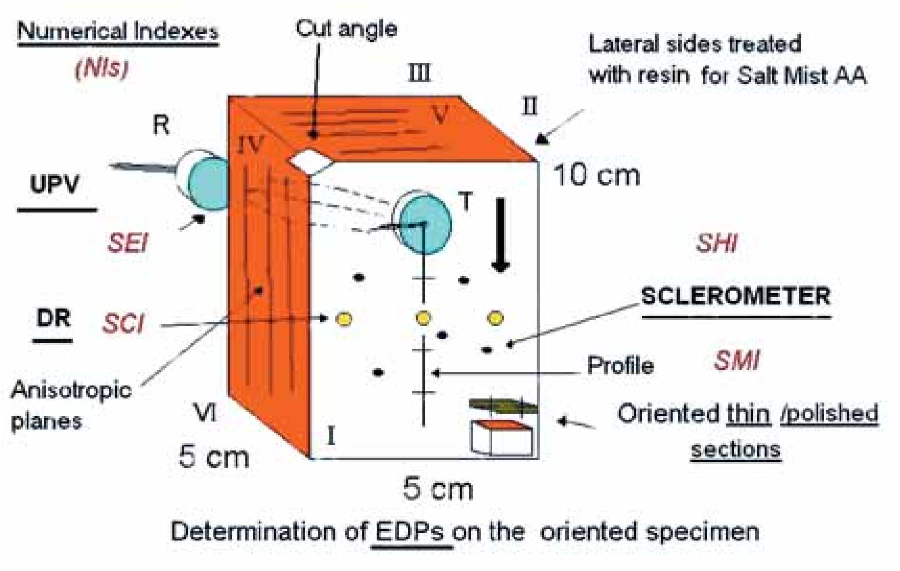

Figure 1: EDP’s defined on the oriented (cut angle) McDUR specimen

2.5 Artificial ageing (AA) and natural ageing (NA) tests

FT – Freeze / Thaw
SC – Salt Crystallisation
SM – Salt Mist (the specimens for this AA have been preliminarily coated with a resin on the lateral sides, see Fig. 1)
TF – Thermal Fatigue