institutions should ensure appropriate measures are taken to put the selection process in the hands of heritage specialists (art historians, curators, conservators, restorers), and not only physics and chemistry scientists.

As far as a LSF is concerned, such developments imply financing a small set of key technical and organisational improvements on an already-funded facility thus demanding only moderate external financial contribution. The building of such a project should strongly benefit from scaling effects for training, design of new experimental set-ups, etc. *Prior to applying for additional support from the EU, LSFs should start by adapting their internal organisation. In particular, participating LSFs should appoint a dedicated officer devoted to heritage activities. Such contact persons are expected to be highly solicited by the heritage community, and answering the day-to-day issues should be regarded a necessary pre-requisite.*

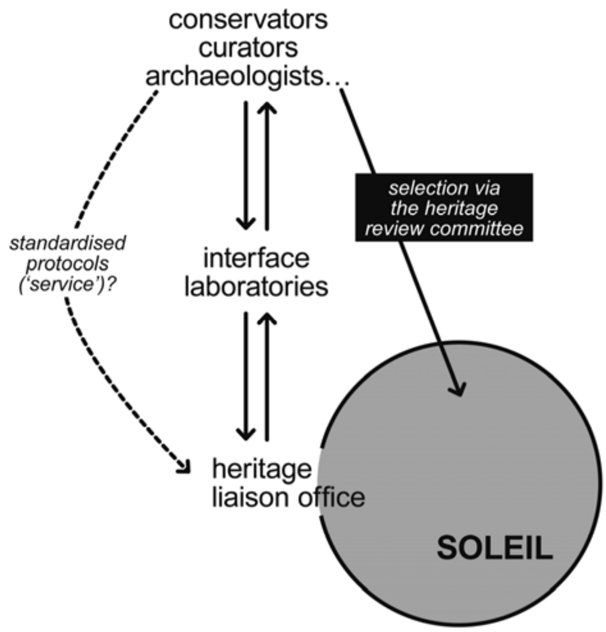

Figure 2: For LSFs, a key step lies in the peer-review process that selects the proposals. In the organisation scheme developed at SOLEIL, the heritage professionals will directly participate to the evaluation of the research proposals. The heritage and archaeology liaison office plays a key role in connecting the facility to the community and interacts strongly with interface laboratories

From the experience developed at SOLEIL, it appears that only a project complying with these major requirements will contribute to answering heritage professionals demand, thus taking into account the specificities of the field with a pragmatic approach and answering the needs at a truly European level.

5 European project details

The SOLEIL European training school on the synchrotron analysis of museum objects was co-organised and funded by:

Non-destructive analysis and testing of museum objects, contract number COST-G8, an international cooperation program within COST – European Science Foundation (ESF), chair: Prof. Annemie ADRIAENS, Ghent University, Belgium.

After the start of operations, access of European users to the SOLEIL synchrotron will be supported by:
IA-SFS, contract number RII3-CT-2004-506008A, Integrating Activity (I3) on “Synchrotron and Free Electron Laser Science” a program for research cooperation within FP6 coordinated by Sincrotrone ELETTRA SCPA, Trieste, Italy.

Early data used for the setting-up of the interface has been collected by:
LabsTech, contract number HPRI-CT-2000-40018, European Research Infrastructure Cooperation Network within Improving Human Potential (IHP) in FP5 coordinated by Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Perugia, Italy.

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Transnational Access to the Louvre accelerator facility (AGLAE)

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Key words: Eu-ARTECH; Transnational Access; artwork studies; conservation; accelerator; analysis

1 Introduction

The Eu-ARTECH programme offers a coherent set of Transnational Access (TNA) programmes for improving the access of European researchers in artwork studies and conservation to relevant facilities that exist in, or are owned and run, by European infrastructures.

Objectives of the Eu-ARTECH Transnational Access are:
- to draw together as many as possible European cultural heritage facilities under the same circle;
- to enable the European user community to have easy and transparent access to a range of advanced resources;
- to offer an integrated, professional and consistent level of support;
- to improve the data products delivered by European facilities;
- to extend the opportunities of the access to users of EC Associated Countries.

Actually, Eu-ARTECH proposes access to two facilities which offer complementary activities:

I – Access to AGLAE (Accélérateur Grand Louvre d'Analyse Élémentaire), a single high-level infrastructure located in Paris at the Palais du Louvre (CNRS-C2RMF), where non-destructive elemental composition studies are carried out with high sensitivity and precision, in a unique environment of art-historians, restorers and scientists having a large expertise on artwork studies and conservation;

II – Access to MOLAB, a unified group of joint infrastructures, located in Firenze and Perugia (UNI-PG, CNR-ICVBC, OPD, INOA), where a unique collection of portable instrumentations, together with competences on methods and materials, is available for in-situ non-destructive measurements. The access is devoted to artwork studies and/or evaluation of conservation-restoration methods, directly in a museum room, or on the scaffold of a restoration workshop or in an archaeological site.

In this paper, we will present the results of the two first years (September 2004-May 2006) of the transnational access to AGLAE.

2 AGLAE facility

The AGLAE laboratory is inside the Research Department of the Centre de Recherche et de Restauration des Musées de France (C2RMF), located in the basement of the Louvre Museum in Paris. The Department is a common research unit of the French Ministry of Culture and CNRS. AGLAE is a unique accelerator in Europe to be directly connected to a museum environment [1, 2].

The ion beam analysis (IBA) experiments which are routinely performed by AGLAE are:

- Particle Induced X-ray Emission (PIXE) [3, 4] – and Particle Induced γ-ray Emission (PIGE) which give access to the elemental composition,
- Rutherford backscattering spectrometry (RBS) which gives access to depth profile [5],
- Nuclear Reaction Analysis (NRA), specially devoted to the analysis of low-Z elements,
- PIXE elemental mappings.

Beam spot diameters are from 20 µm to 500 µm [6, 7]. For expert users, more sophisticated and critical experiments can be also performed after agreement with the AGLAE team.

The duration of each type of measurement is variable:

- for a common PIXE-PIGE experiment between 5 and 30 minutes are necessary, depending of the nature of the material and the sensitivity required,
- for RBS or NRA, the average duration is 15 minutes,
- for an elemental micromapping, a typical acquisition time is between 2 and 4 hours.

The ion beam analysis technique are non destructive; a large set of cultural heritage materials can be analysed directly and without sampling: metal, glass, paper, ink, ceramics, painting, stone gem etc.

3 Transnational Access

3.1 Selection procedure

Typical users for access to AGLAE are scientists who usually carry out research on constituent materials of movable artworks, devoted to the study of the manufacturing techniques for a contribution to art-historical studies, or devoted to the characterisation of the artwork conservation state or to establish the effectiveness of a conservation treatment.

The proposals are evaluated by the AGLAE Peer Review International Committee, constituted of: Pr. Annemie Adriaens, Department of Analytical Chemistry, University of Ghent, Belgium; Pr. Aurelio Climent-Font, Universidad Autónoma de Madrid; Dr. Patrick Trocellier, Research Center of Atomic Energy Commission (CEA), Saclay, France and Dr. Jean-Claude Dran as the representative of the AGLAE infrastructure.

Each semester, 7 to 10 projects – originating from Italy, Spain, Austria, Germany, Romania, UK, Belgium, Greece and Norway, for the last two years – were accepted by the Peer Review Committee.

3.2 Access activity during the last two years (September 2004 – May 2006)

A total of 89 days of beam time was allocated to access activity, corresponding to 24% of the available time.

For the June 2005 – May 2006 period (2nd year), this corresponds to 17 experiments (table 1) and a one-day tutorial session for data acquisition and processing in PIXE mode. In average, each experiment received 3.9 days. The experiments were performed by 14 scientific teams, among whom 3 teams had 2 runs and 11 ones one run. The following graphs illustrate the evolution of the access activity from the first to the second year of the programme.

Figure 1 clearly shows the marked increase of beam time allocated to access users to the expense of the infrastructure internal users. The fraction of beam time devoted to access activities was 12% of available time (or 14% of effective experimental time) the first year and respectively 27% and 32% the second year.

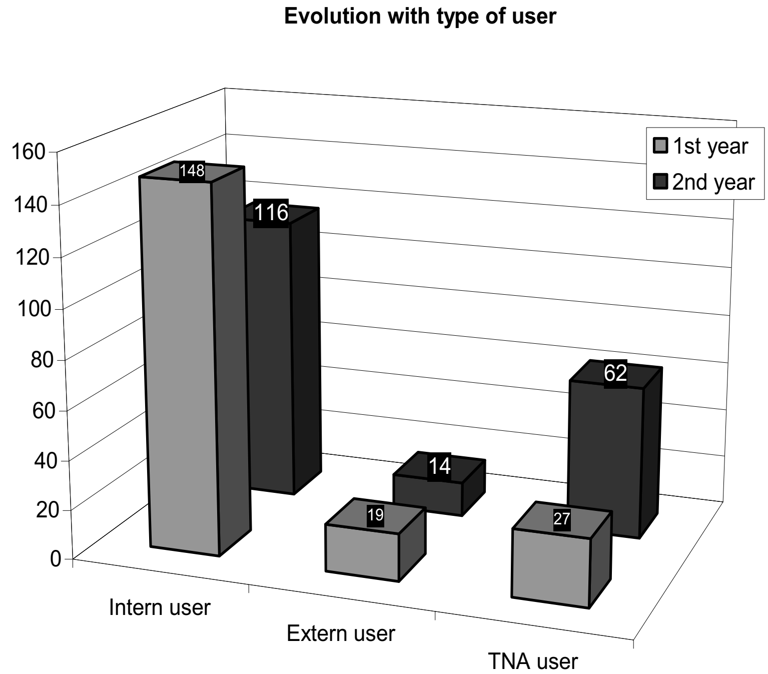

Figure 1: Number of days of beam time allocated to the different users

Figure 2 shows the corresponding increase of the number of experimental runs, of the scientific teams who received beam time and of the different countries to which they belonged.

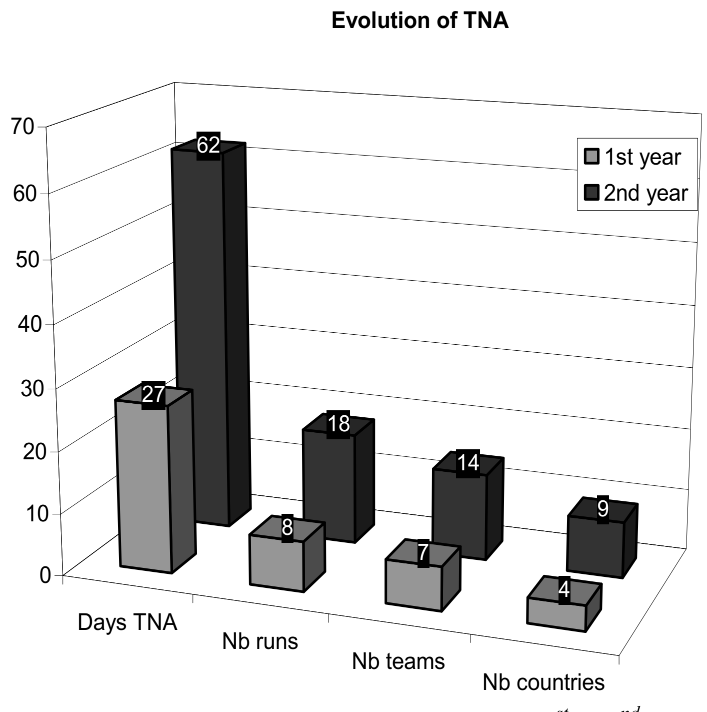

Figure 2: Evolution of access activity from 1st to 2nd year

Figure 3 shows that the mode of operation of AGLAE has remained quite stable, with proton and PIXE highly dominant as respectively the type of probing particle and analytical technique. This is true for both the overall activity and the access activity.

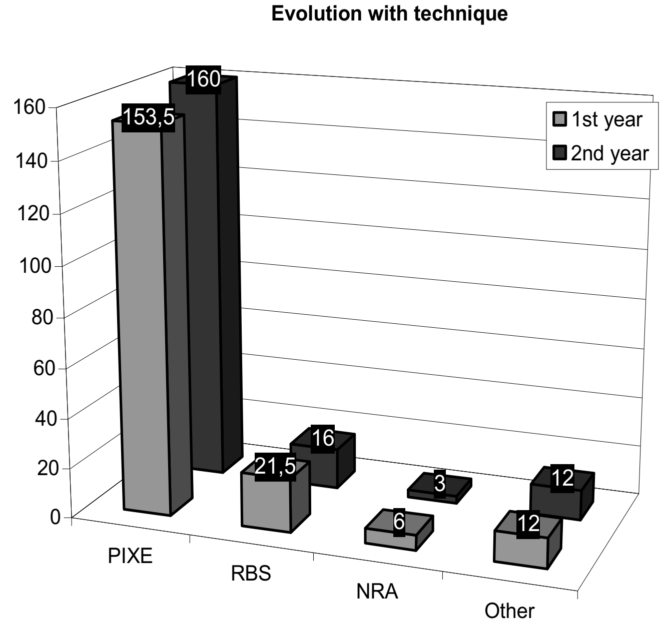

Figure 3: Overall AGLAE activity in days according to the type of analytical technique

The trends exhibited by the figure 4 show the repartition of access beam time with the type of material. One notes a stable beam time for ceramics and drawings but a marked increase for metal (corresponding to several projects devoted to archaeological gold), stone (one project dealing with obsidian), glass and enamel and several materials grouped under the label "bio-organic material" which are varnish and paper-like materials. Under the label "diverse" is indicated the one-day tutorial run dedicated to the GUPIX school.

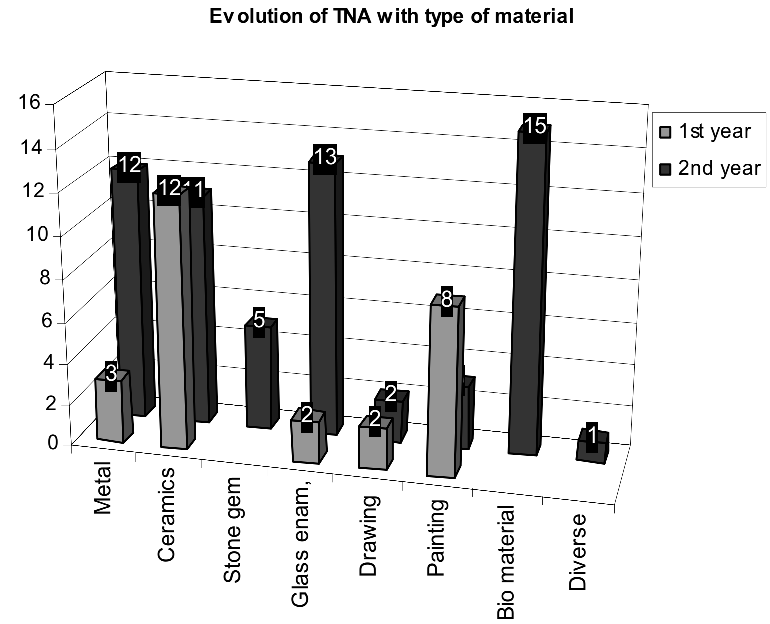

Figure 4: Repartition of access beam time with type of material

4 Scientific output and research results obtained by the user projects

The project achievements are summarized in table 2. The key achievements of the projects are summarized in chronological order of the individual beam time runs (the *project leader* is printed in bold).

The first project carried out by *V. Adrymi-Sismani* in June 2005 was concerned with the analysis of gold foils and objects coming from the tomb of Akrotiki in Greece. 18 objects were analyzed by PIXE and PIGE; furthermore 6 objects were analyzed by PIXE-XRF, a variant of XRF enabling a better limit of detection for Pt. Groups of objects with different trace elements compositions were recognized.

The second project in June 2005 dealt with the study of glass chandeliers from the Nostetangen Glassworks factory in Norway by PIXE and PIGE. *A. Björke* has brought the objects to AGLAE. 110 spectra were acquired in this run. Different types of glass used for chandeliers were identified.

Another project used the PIXE and RBS techniques to analyse the lustered ceramics from Triana / Seville, Spain. In this project specific techniques of the ceramic workshops of Triana were identified through the study of archaeological objects. Since the luster layer was inhomogeneous, beside point analyses, mappings were also made. Results of this and earlier runs were presented to the IBA 2005 Conference in Seville [8]. The projects headed by *A. Polvorinos* on lustered ceramics got a second run in the AR2 period. In this run ceramics from Cordoba, Andalusia were analysed by PIXE and RBS to complete the knowledge on the Iberian the lustre production techniques of the 13th-15th century.

To insure the security of curators dealing with dried botanical collections the content of hazardous inorganic elements of an herbarium was analyzed. V. Purewal and *B. Colston* have brought herbarium samples from the National Museum of Wales which were analyzed by PIXE (points and mappings). The aim of this study is to find an easy way and accessible to every museum to estimate the hazardous potential of these collections, e.g. by utilizing UV-light. The As, Pb and Hg contamination of the herbarium paper sheets was determined. This project received a second run in the AR2 period to complete their investigations on dried botanical collections by PIXE. A large database has now been built on the potentially hazardous elements contained by their collection.

A project concerning violin varnishes was carried out by *A. von Bohlen*. On small wood / varnish samples µPIXE mappings were done to estimate from the elemental distribution the presence of multiple varnish layers applied by the Italian Masters of string instruments of the 18th century. The publication of these results will be published [9]. *A. von Bohlen* got a second run in the AR2 period for a new project. His objective is to obtain more quantitative PIXE measurements in organic matrices like paper, wood or fabrics, by using internal standards. A series of tests was performed, using droplets of calibrated solution mixed with ink on different paper and parchment supports. The validity of the such an approach will be verified by chemical analysis of the treated paper samples.

Continuing the work on the ceramic workshop of Mastro Giorgio *G. Padeletti* has analysed two objects from the Town Museum of Gubbio, Italy and two objects from the Louvre museum. PIXE and RBS were used to get more data concerning the Gubbio lustered ceramics production. The results of this run and the previous one has led to publication [10].

Another project dealt with the analyses of excavated glasses from the site of San Martino di Ovaro (north-eastern Italy). The samples belonging to different periods of this site, a paleo-

Christian church (5^{th}-10^{th} centuries) and a market place (12^{th}-16^{th} centuries), were brought by *A. Zucchiatti*. 142 points were measured by PIXE to attribute these glasses to different production periods or production centres.

In a project on corrosion of historical glasses submitted by *M. Schreiner* a feasibility test was made with altered glass samples. Non-vacuum ERDA was used to estimate the thickness of the hydrated layer on the surface of a reference glass. The samples were analysed by M. Maeder and were also studied by other methods like ^{15}N-NRA in another laboratory.

The last experiment carried out in the first semester of the AR2 period concerned ion beam induced luminescence (IBIL) and its application to the field of cultural heritage. A wide range of pigments and varnish materials were analyzed by *A. Quaranta* to gain a better understanding of the process and to find the best experimental parameter for ion beam induced luminescence spectroscopy. A database containing IBIL spectra is acquired. The first results have been reported in an international conference and will be published in the proceedings [11].

A project aiming at developing a protective sol-gel coatings for ancient glasses and enamels conducted by *R. Bertoncello* received the opportunity of a second run in view to determine the thickness of sol-gel layers by RBS. The users obtained interesting results on the effects of the catalyst used for the production of the protective coating and on the effect of weathering on the thickness and stability of this coating. These results were compared with results obtained in a previous run carried out in the AR1 period. The first data obtained have been reported in [12].

Trace element analysis of the gold from Visigothic “Pietroasa” gold hoard was performed in order to get insights on the gold's provenance. Therefore PIXE mappings and spot measurements were done. It was possible to distinguish groups with different trace element compositions. Worth mentioning is the discovery of Ta inclusions in the gold of a Germanic fibulae. This project led by *B. Constantinescu* already received beam time in the period AR1. The results were presented at the 36^{th} International conference on Archaeometry (April 2006, Quebec, Canada).

Elemental analysis of Sardinian obsidian by PIXE aimed at determining the provenance and at finding correlations with certain types of artefacts, was performed by *C. Lugliè* and co-workers. Specificities in knowledge of the preferred obsidian type used in early Neolithic Sardinia were obtained.

A large collection of fine silverpoint drawings kept at the Albertina museum in Vienna will be investigated using the VERA ion beam facility also located in Vienna. A project for access to AGLAE submitted by *R. Golser* intends to determine the best experimental parameters for the analysis of metal point drawings to avoid damage by the incident beam. In the run performed, a series of samples of Hadernpaper was bombarded with protons under various conditions, to check the absence of visible damage on the drawings which will be analysed. The project already received beam time in the AR1 period.

A project aimed to better understand the properties of antique bronze patinas e.g. colour, resistance has been submitted by *D. Strivay*. The PIXE and RBS techniques will be used to analyse samples during a run scheduled at the end of May 2006.

Finally, the first users meeting was held on November 2005 at the C2RMF in Paris. 74 participants were present, originating from 11 European countries Italy, France, UK, Portugal, Netherlands, Czech Republic, Germany, Belgium, Spain, Greece, and Malta.

Table 1: List of experiments performed during the semester June2005 – May 2006

Project title	Field	Applicant	Institution	Country	Beam time (days)
Provenance of gold from Kasanaki tombs (a)	metal	V. Adrymi-Sismani	Dir Antiquités Volos	Greece	4
Glass chandeliers from Nostetangen (a)	glass	A. Bjorke	Norv. Inst Cult. Heritage	Norway	2
Lustered ceramics from Sevilla (2)	ceramics	A. Polverinos	U Seville	Spain	3
Analysis of hazardous organic and inorganic residues applied to dried botanical collections	organic material	B. Colston	U Lincoln	UK	4
Elemental analysis of historical violin varnishes	organic material	A. Von Bohlen	Inst Anal Sci Dortmund	Germany	4
Study of materials and techniques of lustered majolicas (3)	ceramics	G. Padeletti	ISMN-CNR	Italy	4
GUPIX school					1
Study of stained glasses from a paleo-Christian church of Friuli	glass	A. Zucchiatti	INFN Genova	Italy	3
Non-destructive evaluation of the corrosion of glass objects and enamels	glass	M. Schreiner	Acad Fine Arts Vienna	Austria	3
Ion beam induced luminescence (IBIL) for cultural heritage (2)	pigments	A. Quaranta	U Trento	Italy	3
Study of sol-gel protectives for ancient glass (a) (2)	glass	R. Bertoncello	U Padova	Italy	5
Micro-PIXE studies on Visigothic “Pietroasa”gold hoard objects (2)	metal	B. Constantinescu	Inst Nucl Phys Bucarest	Romania	3
Neolithisation and obsidian circulation in Western Mediterranean occidentale: early phase of Sardinian Neolithic	stone	C. Lugliè	U Cagliari	Italy	5
Damage evaluation for Micro-PIXE used for the analysis of metal point drawings	drawing	R. Golser	U Vienna	Austria	2
μPIXE analyses of elements in paper, parchment and wood. A feasibility study	organic material	A. Von Bohlen	Inst Anal Sci Dortmund	Germany	5
Analysis of hazardous organic and inorganic residues applied to dried botanical collections (2)	organic material	B. Colston	U Lincoln	UK	2
Analyses of lustred ceramics from Andalusia (3)	ceramics	A. Polvorinos	U Seville	Spain	4
Study of antique bronze patina	metal	D. Strivay	U Liege	Belgium	5
				Total	62

(a) Project accepted the previous semester and slightly delayed
(2) (3) The figures indicate that the experiment corresponds to a second or a third run of the same project.

Table 2: Project achievements

Amount of access	Scientific field	Acronym/Project Title	User-Project Objectives	Achievements
4	Archaeological gold	VOLOS GOLD: Provenance of gold from Kasanaki tombs	Trace element analysis of the gold fragments to find the gold’s provenance	Differentiating groups with different trace elements compositions
2	Glass	NOSTETANGEN GLASS: Glass chandeliers from Nostetangen	Differentiating glass types used at the Nostetangen glassworks	Identification of different types of glass used for chandeliers
7	Ceramics	LUSTRE: Lustered ceramics from Seville	Characterisation of archaeological lustered ceramics	Glaze and lustre composition of Hispano-Islamic ceramics
6	Botanical collections	HERBARIUM: Analysis of hazardous organic and inorganic residues applied to dried botanical collections	Evaluation of the potential health danger of the handling of dried botanical collections	Determination of the As, Pb, Hg contamination of herbarium paper sheets
4	Musical instruments	VIOLIN VARNISH: Elemental analysis of historical violin varnishes	Finding technological differences of certain workshops in applying varnish	Identifying varnish layers on samples from different workshops
4	Ceramics	MAJOLICA: Study of materials and techniques of lustered majolica	Insight on techniques of production of majolica	Specificities in composition of glazes of Italian majolica
3	Glass	STAINED GLASS: Study of stained glasses from a paleo-Christian church of Friuli	Attribution of glass fragments to certain production side i.e. local or imported production	Identification of two different types of glass natron glass and vegetal ashes glass
3	Glass	GLASS CORROSION: Non-destructive evaluation of the corrosion of glass objects and enamels	Feasibility study of extracted beam ERDA on corroded glass samples	Determination of hydrated glass surface layer after an acid attack
3	Pigments	IONOLUMINESCENCE: Ion beam induced luminescence (IBIL) for cultural heritage	Improve the analytical capabilities of IBIL in the field of cultural heritage	Compilation of a IBIL database for materials of cultural heritage
5	Glass	SOL GEL: Study of sol-gel protective for ancient glass	Development of protective coatings for glasses and enamels	Determination of sol-gel layer thickness after different sol-gel preparation methods
3	Archaeological gold	VISIGOTHIC GOLD: Micro-PIXE studies on Visigothic “Pietroasa” gold hoard objects	Trace element analysis of the gold fragments in order to find the gold’s provenance	Differentiating groups with different trace elements compositions
5	Archaeological stone	OBSIDIAN: Neolithisation and obsidian circulation in Western Mediterranean occidental: early phase of Sardinian Neolithic	Elemental analysis of obsidian in order to find correlations with certain types of artefacts and to determine the provenance	Specificities in knowledge of the preferred obsidian type used in early Neolithic Sardinia
2	Drawing	METAL POINT DRAWING: Damage evaluation for Micro-PIXE used for the analysis of metal point drawings	Insights on the safe range of beam parameters before damage occurs on prepared rag paper	Series of Hadernpaper after being bombarded by protons under various conditions, to be aged artificially
5	Improvement of accuracy	INTERNAL PIXE STANDARDS: µPIXE analyses of elements in paper, parchment and wood. A feasibility study	Development of a new quantitative analytical method for inorganic elements in an organic matrix.	Test series of standard solution droplets on different paper and parchment supports
5	Metal	BRONZE PATINA: Study of antique bronze patina	Better understanding of the properties of antique bronze patinas e.g. colour, resistance	Will be done in May 2006

5 Conclusion

This transnational access gives the opportunity to European conservation scientists, conservators / restorers, or conservators to carry out ion beam analysis on materials of culture heritage. After two years, the transnational access activities have now reached their normal status. Results of the experiments are already published or in press.

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MOLAB (Mobile Laboratory): a Transnational Access service for in-situ non-invasive studies of the European cultural heritage

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The mobile laboratory, MOLAB, consists of a unique collection of twelve portable instruments, devoted to carry out *in-situ* non-invasive studies on artworks directly in a museum room, in a conservation / restoration laboratory or even in an archeological site. The laboratory is part of the programs of Eu-ARTECH (www.eu-artech.org), one of the Integrated Infrastructure Initiative of the 6th F.P.

The equipment belongs to four joint Italian institutions (namely SMAArt, OPD, CNR-ICVBC, and CNR-INOA) and is fully vailable to interested users (scientists, curators, conservators) for Transnational Access services upon specific application. Selection procedures are analogous to those currently applied for access to large scale facilities.

MOLAB is composed by a compact micro-Raman, a fiber optic mid-FT-IR spectrometer, an XRF device, a high resolution colour-IR reflectograph, a laser micro-profilometer, a MOUSE® NMR relaxometer, a portable fluorimeter, and other systems.

Since July 2004, MOLAB has made possible to carry out *in-situ* studies on precious artworks, such as the *Madonna Litta* and *Madonna Benois* by Leonardo at the Hermitage Museum in St.Petersburg, the *Vergin of the Rocks* by Leonardo at The National Gallery of London, the *Lamentation on the dead Christ* by Bronzino at the Museum of Fine Arts and Archeology in Besancon, the majolicas of Mastro Giorgio (XVI century) at the V&A Museum in London, the mural paintings of the XIV century at St.Euthimios in Thessaloniki, and others. Relevant results will be presented at the conference.

Wind tunnel modelling in conservation

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Key words: wind effects, historic structures, wind-rain loading, climatic factors

1 Introduction

Historic buildings and objects of high values are subjected to climatic actions that can last either over many years or that may have a local and short temporal character. It is generally understood that these changes have a wide range of direct and indirect effects on the historic built environment and that they may cause serious damage or deterioration due to change of temperature, humidity, pollutants and other factors and naturally because of erosion processes caused mainly by wind flowing in a specific manner around body [1]. In the ITAM ARCCHIP, some aspects of the exposition of particular historical buildings and their valuable details that suffer from many negative influences of today's climate are studied. Three different topics are presented in the article. First, a study of the hydrophobisation effects on the sandstone by modeling the action of driving rain on aged stone statues is presented. The exposure of two samples to the combined effect of the rain, wind and low temperature cycles in a climatic wind tunnel aimed to reproduce accelerated exposure to natural climatic actions. Second, an experiment was performed on two scaled models of selected church towers in the Boundary Layer Wind Tunnel. The pressure and wind velocity measurement serves primarily as the prototype for the subsequent numerical models, which can be used for parametric studies. Third, an experimental object modeling the Czech National Museum has been built and tested. A feasibility study of pollution soiling of historical building facades was also undertaken in a large environmental wind tunnel.

The experiments described in this article were carried out in a climatic wind tunnel "Jules Verne" in Nantes, see Fig. 1 and in BLWT in Prague. This experimental facility has been used for studies of influences of combined climatic factors typical for real situations [2, 3].

One of the advantage of the climatic wind tunnel facility is the possibility to simulate and control the combinations of climatic parameters to perform tests on a full scale basis which is often the only relevant experimental scale. In order to offer the widest range of simulation possibilities, two different circuits were built: The external ring called dynamic circuit (or unit) enables the reproduction of the spatial and temporal evolution of natural wind up to an average of 100 km/h in the environmental test section. The modelled air flow can be associated with rain (up to 250 mm/h) or sand storms (the sand concentration can reach 10 g/m^3 in a 10 m^2 section). The highest air flow speed of 280 km/h is reached in the cyclonic test section. The equipment of this test section includes a six component balance associated to a turntable and a boundary layer trap. The total power of the adjustable pitch fan is 3200 kW. The internal ring called thermal circuit (or unit) can reproduce thermal changes from -25 °C to +50 °C and relative humidity from 30% to 100% in the test chamber whose cross section is 70 m^2. According to the section of the adjustable nozzle, the maximum air flow speed can be set from 90 km/h to 140 km/h.

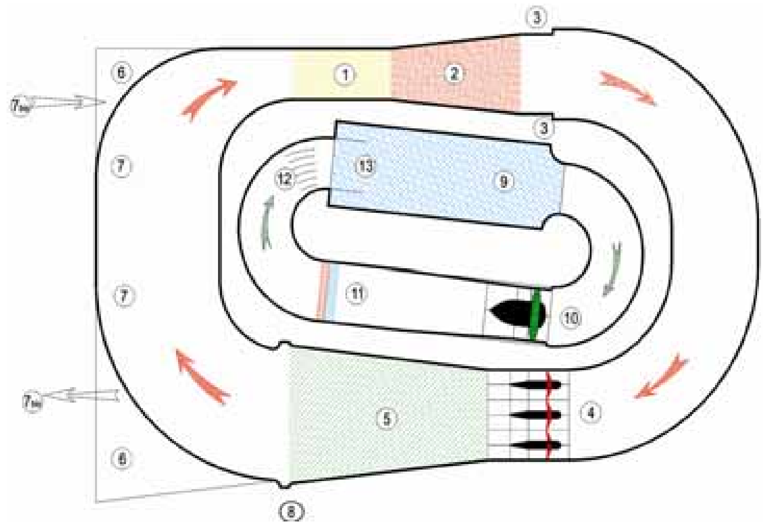

Figure 1: Two climatic circuits of the climatic wind tunnel Jules Verne at CSTB Nantes

Snow guns are used to produce a thick snow mantle (15 cm/h) on the 200 m^2 floor of the test chamber. The snow quality related to the snow water content is adjustable. Other climatic parameters as frost, fog, hail and solar radiation can be reproduced. A roller bench (250 kW) whose rotating speed is linked to the wind speed and a burnt gas extractor are dedicated to automotive testing. The total electrical power necessary to run the thermal unit is 3000 kW divided in 1000 kW for the fan and 2000 kW for the cooling system.

2 Experimental investigation of gothic sandstone pinnacles subjected to combined climatic loading

The penetration of water into material, mechanical damage due to frost, crystallization of new minerals or severe temperature and moisture changes represent crucial problems from the degradation point of view and are considered to be worth to study under real or simulated conditions. During four day lasting exposition of gothic pinnacles from one of the most important gothic late medieval churches – St. Barbara in Kutná Hora (Bohemia) – an efficiency of water repellent (hydrophobic) surface coat was verified in the wind tunnel. Further, the temperature and humidity changes on the surface as well as inside the stone elements have been measured during different climatic situations modelled in the wind tunnel.

Two authentic pinnacles made from local and typical Kutná Hora calcareous sandstone were tested. They were dismantled in the course of restoration of the church due to their high deterioration and replaced by replicas cut from new stone. Their deterioration has been caused by physical as well as chemical corrosion processes combined with the temperature fluctuations and cyclically changed gradients inside the volume of the studied elements. The chemical corrosion of stone is further affected by water acting as a reaction as well as transport medium [3].

2.1 Experimental set-up and methodology

The shape of pinnacles is shown in Fig. 2 and the characteristic dimensions of the all stone pinnacle and the second with an iron rod on the top were respectively: the height of 1290 mm and of 870 mm, the base of 300 × 300 mm (cornice 450 × 450 mm) for both pinnacles, the top of 70 × 70 mm and of 130 × 130 mm respectively. The cross flower had a base of about 560 × 560 mm before damage and the thickness of about 170 mm. The all stone pinnacle was restored before the tests in a way which has been used for the restoration of the St. Barbara Church.

After a cleaning, the stone was locally solidified by means of an organo-siliceous injection (IFEST OH), the damaged parts and cracks were filled either with white cement based mortar or with mastic bound by a silicic (acid) ester agent and finally the whole surface was covered with the hydrophobic organo-siliceous agent (IMESTA IW 290). The second pinnacle has been left in its original state without any conservation intervention.

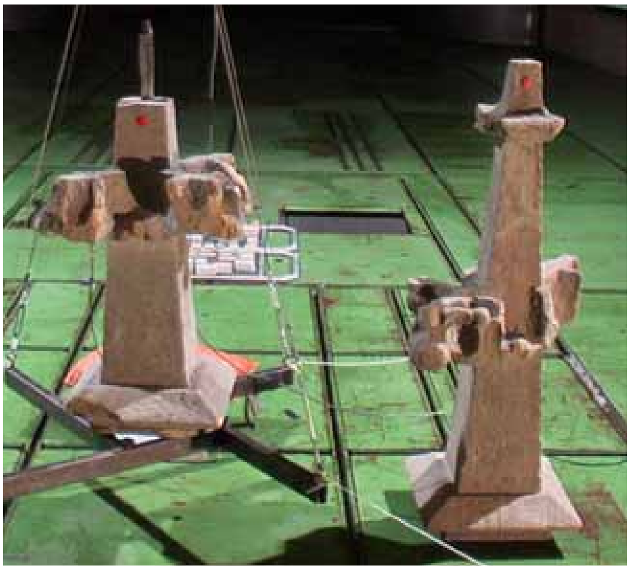

Figure 2: Specimens prepared for tests in the wind tunnel

During the tests, several combinations of climatic loading factors were applied. These combinations included temperature, rain and wind speed. The temperature was either kept constant at 5 °C or it cycled between +5 °C and -5 °C. The rain was introduced in the airflow up-stream in the test section by a rain system made of five pipes. Seventeen calibrated rain nozzles were fitted on the pipes. According to the wind speed settings, the water pressure was set to a defined value in order to produce visually uniform water spreading in the test section. When the testing conditions were stabilised, the total water flow was measured. Only two wind velocities were utilized: 5 ms^{-1} and 10 ms^{-1}. The temperature and humidity inside the stone was continuously measured by means of one NiCr thermocouple and two combined temperature/relative humidity sensors Ahlborn FHA 6461. They contain capacity RH sensor with span of 0-100 % of R.H. and accuracy 2 % R.H. and a temperature sensor Ntc of the type N with accuracy of 0,1 °C in arrange of -20 °C to +80 °C. The data were read and recorded by means of a data logger ALMEMO 2290-8.

The temperature on the surface of the stone during „accelerated life cycles“ was measured by the IR thermovision with a very high sensitivity, which helped in understanding dynamics of thermal changes on the surface.

The weight of the pinnacles was measured during weathering cycles by means of a special hanging balance designed and prepared for the purpose of the tests.

2.2 Experimental results, water penetration into the gothic pinnacle samples

The surface of gothic pinnacles has its natural water repellent characteristics much higher than the fresh stone. Some complementary tests were carried out in our laboratories at which the water sorption and wettability were measured by means of Karsten tubes. According to the assumptions the water absorptiveness of the treated pinnacles was zero during 5 minute measurements. The wetting property investigation proved that the water repellent treatment is not continuous and some parts have water-receptive (hydrophilic) features. It was well apparent on thermograms after rain or on the pictures with rain water visibility agents. This explains small measured weight increase which appeared after rain at treated pinnacle, too. During the water penetration tests also the amount of water adherent to the surface after rain in the form of drops was estimated in order to be able to correct the weight measurements in the wind tunnel.

On the other hand, also the untreated pinnacles had quite low water absorption. The water absorption coefficient after 18 minutes was equal to 0.93 $kgm^{-2}h^{-1}$. This phenomenon explains a relatively low water penetration during the wind driven rain into the untreated pinnacle and the following low difference between the treated and untreated elements. The wettability of the untreated pinnacle was much higher than that with hydrophobic paint.

The effect of hydrophobic protection can be well compared in the Table 1 where the weight gains after wind driven rain on treated and untreated pinnacles are summarized. The rate of water penetration decreases with the rain duration due to partial saturation of pores. It was further observed that water flow along the vertical surface probably has a drag effect which decreases capillarity and reduces the wind effect.

Table 1: The effect of hydrophobic coat on the original gothic pinnacles

Rain driving wind speed of 10 ms^{-1}	Increase of the weight due to rain (% w)	
Rain duration	Unprotected surface	Water repellent protected surface
60 min	0,92	0,20
+135 min	1,86	0,82
+ 60 min	-	0,93
+ 60 min		0,98

From the paragraphs above it follows that hydrophobic treatment on the fresh stone samples (with more open pores) and brick leads to a higher protective effect compared to the effect on old weathered stone. The ancient stone elements have an apparent “natural” protective layer on their surface at least in some areas. The changes of relative humidity measured inside the stone reacted to the temperature variations ± 5 °C rather than to the moisture content in the stone and it attained values of about 3%.

2.3 Surface temperature measurements

Surface temperature changes of the pinnacles were recorded by means of infrared camera. One example of a sequence of measurements during cyclic change of climatic parameters is given in Fig. 3. This case was aimed to study the effects of wind on temperature and moisture content changes in the treated pinnacle after 2 hours of an intensive rain. From this figure it follows that wind substantially influences both the distribution of surface temperature and the absolute temperature compared to the ambient temperature. Of course, the decrease of the temperature under the level of surrounding air ones is significantly influenced by the evaporation of water from the wet stone. Further, the mass volume dependent inertia and heat accumulation effects are also well visible. The experiments proved that subtle parts of stone elements, especially when wetted are subjected to more severe temperature differences and related temperature gradients than massive parts, which might lead to initiation and opening of fissures and cracks, resulting in material damage and degradation.

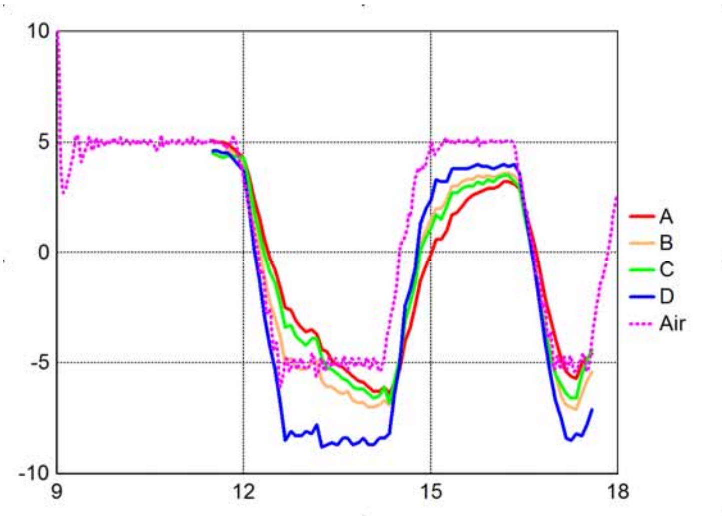

Figure 3: The differences in surface temperature in the course of surrounding temperature cycle. The lines A,B,C,D correspond to the points on pinnacle SP01, SP02, SP03, SP04

The infrared measurement of surface temperature can be further utilized for study of flows and eddies around the complex architectural shapes. Wetting the surface intensifies the measured effect.

2.4 Temperature inside the pinnacles during cyclic climatic loading

When compared to the surface temperature, a much more significant difference and related temperature gradients were identified. The surface data were taken from the thermovision measurements in the areas near to the sensor measurements. The real temperature gradients in structures are dependent on the long term conditions of the surroundings of a building. The most dangerous are sudden changes, in many cases accompanied with precipitation, which further increases the damaging mechanisms, especially in stones the volumetric stability of which is moisture dependent, (namely some sandstones).

The wind tunnel measurements was completed with some laboratory tests at which the temperature change inside a small cube of dry and wet sandstone was investigated during a loading cycle in a range of ± 20 °C. Similar curves and dependencies were measured.

3 Wind load damage to the historical structures

The air flow effects on open-air located historical structures or sculptures could be quite disparate. In effort to systematically describe their negative impacts for purpose to anticipate hypothetical risks we may define two basic groups of possible failures which fundamentally differ in their causal relations [6, 7].

Firstly a deterioration caused by the wind erosion needs to be mentioned. Weathering processes affect not only geological and natural formations but also the far most of building materials if they are exposed to climatic conditions. Ever so little breeze can waft small parts of hard solids like e.g. sand. After a long term action the abrasive impact could be very strong bringing on significant changes of all exterior parts of structures. On the other side there are also some positive aspects of such changes. Many a time the authentic impression of ancient architecture is emphasized just by its gentle weather-worn look. In the process of proper maintaining the cultural heritage monuments the one of the most difficult tasks is to find right balance between sustainable technical conditions and appropriate presentation.

The second group of damages relates to critical exceeding of bearing capacity of construction materials by wind loading. An acute enhancement of material stress can cause local mechanical damages or in case of extreme events (windstorms, hurricanes) even grow to collapse of structures. A character of such incidental causes is mostly sudden and unexpected, so the precautionary actions are much more difficult. Strong winds and storms cause damages and failure on both the cultural and natural heritage.

3.1 Historical excursion

In the past the serious damage to buildings caused by climatic reasons - windstorms, hurricanes or floods – definitely belonged among the most remarkable events to be noted in chronicles and other written sources. Together with large fires, often started by thunderstorms, they make the numerous groups of records in chronicles. As the actual results of historical research shows, the windstorm damages of roofs were recorded relatively often in the past, (see Fig. 4). We can understand that the damage descriptions might have been exaggerated and some times even overestimated on purpose to obtain funding for repairs more easily. On the other hand the detailed and reliable descriptions of particular incidents are very valuable for defining the weak points of typical building structures. Churches with their high roofs and in particular steep spires represent the largest group of buildings mentioned in written sources [5]. Outlook towers with timber structures on the tops of the hills and standing for the most part separately from the traditional settlements were maybe the most endangered building type, especially around the 1900. Quite surprising is the report from 1842, which speaks about the menhir in Klobuky (Central Bohemia) falling to the ground due to a hurricane. To this category we include also the failure of freestanding walls, as e.g. attic gables, ruins, fencing walls etc. Most of the damage caused by strong winds touched the roof covering. Wooden shingles were in this sense much more resistant than for example ceramic or slate tiles. Copper sheets when used in pitched roofs of a larger extent caused serious problems too. The total collapse of an all-timber structure of a roof spire was generally not the result of structural faults in timber construction but was connected with longer established existing problems, as for example rotten wall plates

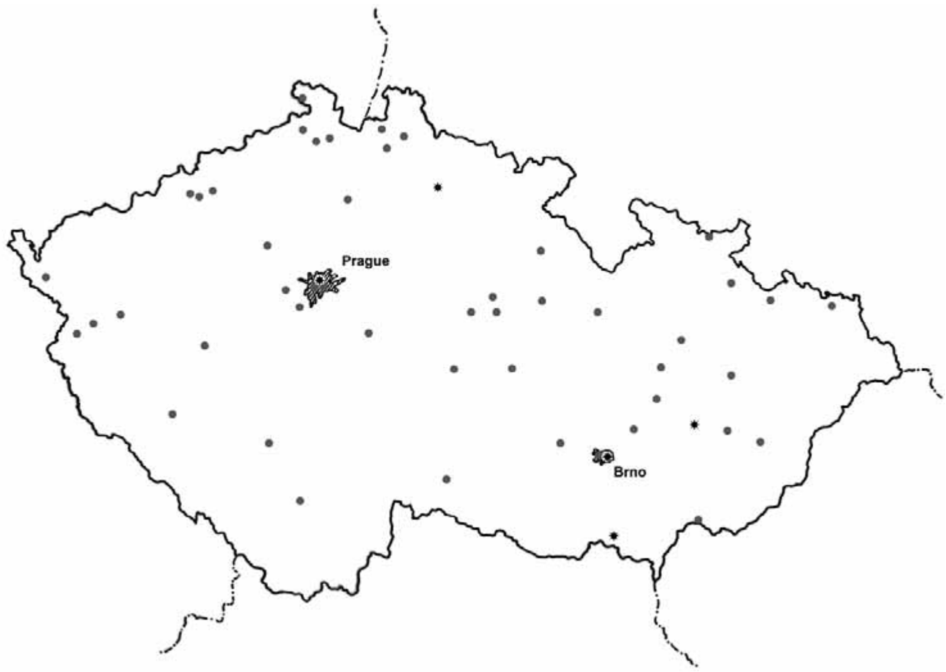

Figure 3: Map of wind damages in the past within historic Czech Lands.
Stars mark the sites experiencing multiple damage of one single structure [4]

or roof leakage. That means that the periodic monitoring of wood condition within the constructions is essential to prevent future damages. A combination with other structural failures – cracking in masonry or vaulting – could be very dangerous leading to a collapse of the building as a whole. Generally, the movement of the air around buildings influences initiation and development of damage due to its motion, too. However, this effect must be treated rather in the weathering group of problems. Baker [1] refers a catastrophic windstorm from the year 1703 which caused only in London 21 deaths, two millions of £damage, (in all UK about 100 millions of £), and which was described in records by the following words: "the streets lay so covered with tiles and slates, from the tops of the houses, especially in the out-parts, that the quantity is incredible, and the houses were so universally stript, that all the tiles in fifty miles round would be able to repair but a small part of it".

3.2 Ranking of structures according to their sensitivity to wind effects

Study of wind effects and an effective design of mitigation measures call for ranking of structures and elements vulnerable to wind effects. The authors suggested the following two categories: wind resistant structures and elements and vibration prone elements and structures, respectively [8]. They may be for example:

1. windows and window glazing
2. architectural elements (e.g. pinnacles); wind releasable elements, namely roof covering
3. structure susceptible to partial damage by wind, such as: roofs, windmills, tall sculptural works
4. structures and elements vulnerable to overall collapse due to wind action, for example:free standing walls and elements (attic gables, ruin walls, fencing walls, chimneys, menhirs, poles, etc.), light and tall buildings (towers, timber houses, etc.), trees.

In many cases the observed damages result from simultaneous action of several factors, wind being only one of them, (see below).

3.3 Numerical solution compared with wind tunnel experiments

From the previous text we may clearly see, that wind together with other synergetic effects may cause serious damage. Therefore better knowledge of the wind flow around structural details

Figure 4: The scaled model posted in the wind tunnel measuring section

and structure itself is an important issue, especially in the need of repair and maintenance. Analysis of the flow around a building is generally very demanding task even for relatively simple geometrical shape.

The numerical solution depends on many parameters among them the kinematic viscosity, wind velocity vector and dimensions of the body is the most significant. It is not intended to represent all mathematical model in this article. Rather we present the results which we observed by using an innovative numerical model. We consider a viscous, incompressible fluid occupying at an instant a bounded region. The velocity and pressure fields modeling is governed by the Navier-Stokes equations. Both the Dirichlet- and Neumanntype boundary conditions are taken into account. The initial condition consists of a specified divergence-free velocity field. Applying lower values of kinematic viscosity we very early finish with the analysis. The global Reynolds number is of order 10^3 and the computation fails shortly after initial time, just after the the flow approaches the structure and sharp corners. Yet it is one of the cases when finite element computations based on the standard Galerkin formulation of incompressible flows can involve numerical instabilities due to the presence of advection terms in the governing equations, and due to using inappropriate combinations of interpolation functions to represent the velocity, pressure and stress fields. The result of this issue is spurious node-to-node oscillations primarily in the velocity field. Such oscillations become more apparent for advection-dominated (i.e. high Reynolds number) flows and flows with sharp layers in the solution. Such instabilities appear also in the standard versions of other discretization techniques such as finite difference and finite volume methods. To stabilize the computations we use the Galerkin / least-square (GLS) formulation, see [9].

With the stabilization terms we may observe significant changes on the stream lines patterns. Though we may observe the efficiency of the stabilization terms in the Navier-Stokes equations by analysing of the results, we cannot be sure that the flow patterns are completely realistic.

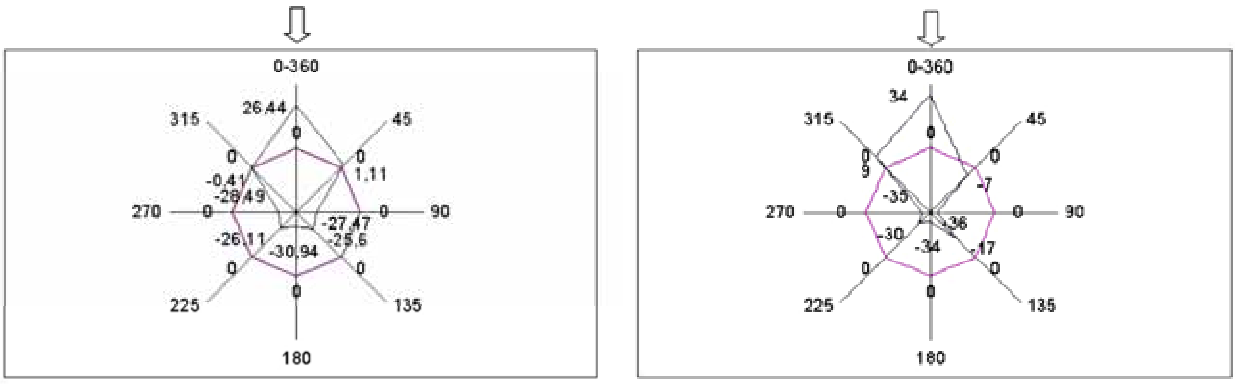

Figure 5: Comparison of dynamic pressures on the spire calculated numerically (left) compared with pressures observed during the measurement

This is common problem in the flow field analysis or aerodynamics. To improve the understanding of the mathematical model the authors have prepared the measurement of the pressures on particular points of the structure (roof, small tower spires). In other words, the so called “calibration” model was designed for the aerodynamic measurement. The inspiration for the model design was taken from the St. Týn church from the Old Town Square in Prague as there are plans toward the wind speed measurement in situ on this tower. The scale of the model is 1:25. The photograph of the model can be seen on the Figure 4. Two wood models of prototype in the scale 1:25 has been equipped with 16 pressure transducers, connected to the roof surface by optimized teflon tubes. The pressures serve as the correction output for the confrontation with numerical studies.

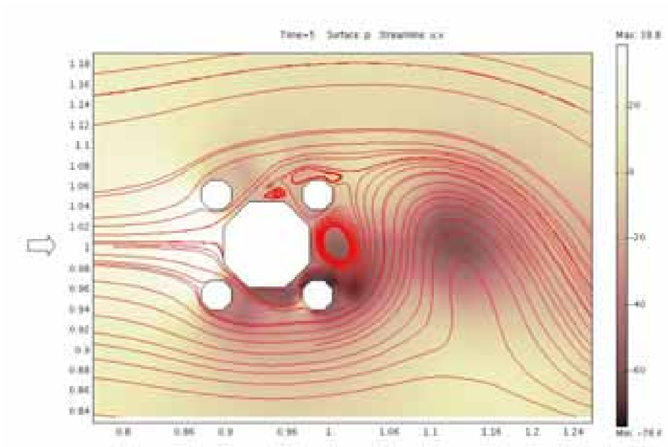

Figure 6: Wind flow patterns calculated numerically and observed in the wind tunnel during flow visualisation experiments

4 Surface degradation of complex architectural form due to atmospheric pollution

The disagreeable appearance of soiled buildings in many larger towns is caused by deposition of particulate matter arising from atmospheric pollution. The deposition of dust particles is characterised by the deposition velocity, similar to gas deposition and on the size of the particles. An experimental object modeling the Prague National Museum has been built and tested. A feasibility study of pollution soiling of historical building facades was also undertaken in a large environmental wind tunnel. Local collectors could trap the dusts carried by the airflow surrounding the building models. This enabled quantitative assessment of facade soiling with respect to the model reduced scale. The building, which is situated to the central part of the Czech capital, is relatively highly exposed to environmental deterioration due to combination of wind, rain, dust and gaseous traffic. The museum is subjected to a long term monitoring and measurements of the dust exposure using special particulate samplers. Though very valuable, this experimental activity needs a long period for both quantification and evaluation of data, so that the experiments have been focused on the speed-up of the whole procedure by means of utilisation of a large environmental wind tunnel.

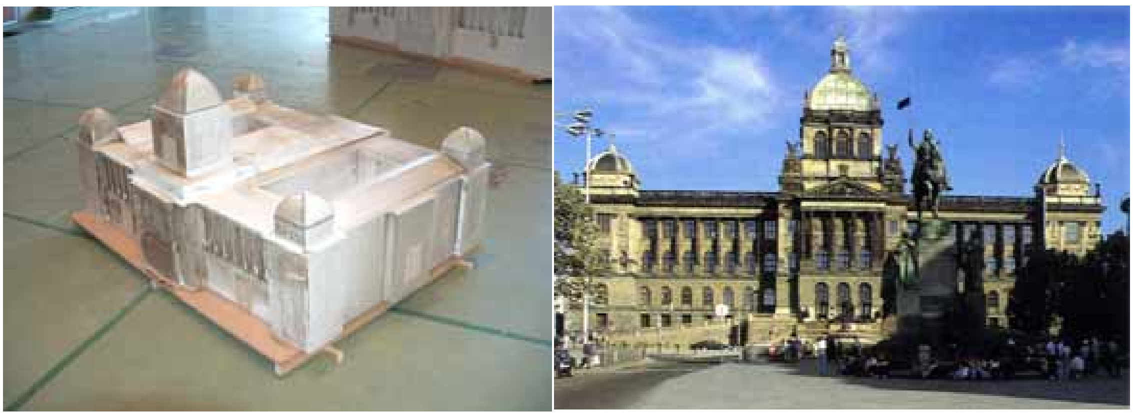

Figure 7: Model of the building (left) and the prototype (right)

4.1 Evaluation of the building inspection

The National Museum is located between two three lane roads with a heavy traffic on the upper part of famous Wenceslas square in Prague. The main façade of the building faces toward the square and one of the roads which separates the object from the square space. The other long facade facing to the East is adjacent to the second road. The Southern and Northern short facades are surrounded with quite quiet areas – a small park and a pedestrian road. Within a larger assessment of the state of the building, all surface structures have been inspected [10] and their damages and failures summarised and analysed. Some of these damages related to the problem of soiling are presented bellow. The building is composed from several blocs around two yards and its roof as well as the main façade are of a complicated shape, moreover decorated with stone sculptures or hard mortar stucco elements.

Significant characteristics of the facade pollution is its variable blackening. It depends on the wind driven rain direction. It is assumed, that the highest intensity of the black color is caused by the wet soiling of the pollutants. Different pollution of the columns at the street side and other sides is obvious. The highest concentration of the dust is on the east side of the building which is washed relatively seldom (Fig. 8). Black colour have also bottoms sides of the roof cornices. As before stone columns are significantly polluted. Main facade is damaged due to wind effect in combination with the frozen water. The large areas of plaster fall off the building.

The museum is subjected in the long run to the measurements of the dust exposure using special sensors (samplers), see e.g. [11]. The corrosion aggressivity on certain measuremnet spots has been assessed by means of decrements of carbon steel and zinc which basicaly corresponds to ISO standard 9223. The results showed that there is big difference between the corrosion on the directly exposed places and the circumferential points.

4.2 Wind tunnel test description

The testing took place in the dynamic unit (environmental test section) of the Jules Verne climatic wind tunnel. The average effective cross section of the test section is 100 m^2. The dust particles (80 microns) were introduced in the airflow up-stream the models by four compressed air injectors. The sand and compressed air injectors were attached to heavy poles placed close to the wind tunnel fans. According to the wind speed settings, the sand concentration was set to a defined minimum value (see test conditions) of in order to produce a uniform spreading around the model. The similarity conditions between the prototype and the mock-up cannot be fulfilled due to inconsistence in two major similarity laws in this case; Froude law and Reynolds number. Therefore, two museum models in the scale 1:40 and 1:80 were placed on the central axis of the test section. Such step allows at least the relative analysis between two scales. The smaller model was located upstream the large model in sufficient distance with respect to the preservation of smooth flow on both bodies.

According to the test specifications, various test configurations were achieved:

Sequence 1: wind direction = West, velocity 5 m/s, concentration 0.41 g/m^3, 15 min,
Sequence 2: wind direction = West, velocity 5 m/s, concentration 0.44 g/m^3, 15 min,
Sequence 3: wind direction = West, velocity 10 m/s, concentration 0.2 g/m^3, 15 min,
Sequence 4: wind direction = West, velocity 10 m/s, concentration 0.2 g/m^3, 15 min,
Sequence 5: wind direction = Southwest, velocity 5 m/s, concentration 0.37 g/m^3, 10 min,
Sequence 6: wind direction = Southwest, velocity 10 m/s, concentration 0.19 g/m^3, 10 min.

Spreading a sticky coating on the model facade collected the deposited dust. Based on the preliminary tests, calculations and similarity requirements, the sand “poudroilite bronze” was chosen. It is a mixture of silicon oxid and aluminium oxid with very small content of Fe_2CO_3 and CaO. Smoke visualisation was also performed. Digital pictures and video recording were taken during the testing and after every single test.

5 Conclusions

The experiments have shown the importance of using a climatic wind tunnel for the historically valuable structures, especially concerning the "accelerated" climatic changes that can be used in calibration and development of models for numerical calculation. Temperature changes are very sensitive to the shape of particular details of complex architectural forms. Further, the cooling and evaporation is highly influenced by the wind flow, especially cold one. Driven rain probably increases the water penetration into the stone only at the beginning of the rain period and after certain saturation the surface water flow rather takes away the water that would penetrate the stone. The moisture content grows by means of infiltration through the stone surface when the ambient temperature increases (high humidity and cold stone surface).

Surface hydrophobic coat quite perfectly protects the stone if applied compactly on the sufficiently large area of interest. However, protection of the stone surface by application of water repellent product has a temporary effect only, which is influenced by the qualities of the treated surface, its performance conditions as well as the selected protective product. Moreover, it seems that its efficiency for protection of weathered surfaces is rather low and its application, therefore, questionable. Some coats even change significantly the deformability and permeability of surface layers which can cause severe material and structural damage.

Surface stone temperatures in wind flow can be measured with appropriate accuracy using thermovision in case of both dry and wet surface. This is because the emissivity of most stone sur-faces (0.85 to 0.95) is not very different from the emissivity of water (0.96). Our technique can be advantageously applied for studying the air flow and eddies around complex shapes and forms. The developed technique can be advantageously applied for study of air flow and eddies around complex shapes and forms.

The article showed the significant influence of the wind load on the structural integrity of historic structures. There are given several examples among many which can demonstrate the damage consequences of the wind effects on particular historical and architectural treasures. The database of the damages caused by the wind is created and available. An experiment on two scaled mock-ups of typical church tower has been prepared. Pressure and flow patterns evaluation will serve as the calibration benchmark for the numerical solution using stabilization technique recently available in other research area.

The pilot experiments dealing with particle deposition in the urban atmosphere were taken out. Optical methods and weighting of samplers has been done in the laboratory. There has been concluded several important points, especially in the relation of confronting the results from the prototype and the models:

- New adhesive sampler has been used with success. They can be used also in further indoor testing only under very specific conditions (short duration of wind event)
- There has been no unambiguous relation between the deposition degree on the samplers on the small and big model and between models and real building.
- Integral effect of the corrosion that is higher on the top of the prototype building was not apparent on the scaled models.
- It is very difficult to assess the influence of the wind speed and concentration of the particles during short time measurement. Moreover wind speed is relatively high so, that saturation of samplers was almost immediate. More experiments are needed in order to understand scale factors and similitude between the prototype and models. However, also accelerated events can be used in computer simulations.
- Though the sampling method is promising, it should be used within the environment with much lower particle concentration and with much shorter exposition time.

- The spectrofotometric method has been used with good results even for the Fe_2CO_3 and CaO, which is rather brown. Anyhow, more colored particulates would give better resolution.

6 Acknowledgements

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CEN/TC 346 Conservation of cultural property

Vasco Fassina

Superintendence to Artistic and Historic Property of Veneto, Italy

Key words: standardization, conservation cultural property, terminology, diagnosis, conservation works

1 Introduction

The foremost aim of European standardization is to facilitate the exchange of goods and services through the elimination of technical barriers to trade [1].

A scientific approach is nowadays essential for the conservation of the Cultural Heritage as preliminary basis to guarantee a proper planning of ordinary and extraordinary maintenance works, as well as to assure their efficacy and durability.

Only thanks to a sound scientific knowledge of the materials constituting the cultural property, of its environmental and conservation conditions, these conservation/restoration works can be successfully carried out.

Unfortunately the great experience developed in this field by the different European countries, for the time being can not constitute a common background because there are too many differences not only in the methods of analysis, but also in the terminology used.

A specific European standardisation activity in the field of conservation of Cultural Heritage is essential to acquire a common unified scientific approach to the problems relevant to the preservation / conservation of the Cultural Heritage.

Moreover, this common approach and the use of standardised methodologies and procedures would promote the exchange of information, would avoid the risk of duplication and foster synergy between the European experts and specialists involved in the preservation activity.

In 2001 UNI, the Italian standardization body presented a request to CEN (Comité Européen de Normalisation) to create a new TC (Technical Committee) dealing with the conservation of cultural property.

The scope of CEN/TC 346 is the standardisation in the field of definitions and terminology, methods of testing and analysis, to support the characterisation of materials and deterioration processes of movable and immovable heritage [2, 3], and the products and technologies used for the planning and execution of their conservation, restoration, repair and maintenance.

In particular, the standardisation activity on the conservation of Cultural Heritage deals with:

- terminology relevant to movable and immovable cultural property, and to the conservation of the cultural property and of the material constituting the cultural property themselves, so that a common European terminology can be created;

- guidelines for a methodological approach to the knowledge of the cultural property and of the materials constituting the cultural property, of the deterioration processes, and of conditions of optimum long-term conservation / preservation work;
- test and analysis methods for the diagnosis and for the characterisation of the cultural property and of their state of conservation with regards to outdoor and indoor environmental parameters;
- test and analysis methods (in laboratory and in-situ) for the evaluation of the performance of the products and methodologies to be used in the conservation work (ordinary and/or extraordinary maintenance);
- test and analysis methods for the evaluation of conservation conditions of indoor Cultural Heritage. In particular, standardisation on transportation and packaging methods, shall take in due accounts the needs and problems related to itinerant exhibitions and exchanges of works of art, in the permanent presentation conditions in museums, galleries, libraries and archives, in temporary exhibit galleries, in stores and in transport packaging.

This standardisation activity will be a useful and valuable occasion to compare, for specific items, different results coming from various European institutions or laboratories.

2 Market Situation in relation to the objectives of CEN/TC 346

The market relevant to the conservation of Cultural Heritage is considerable and it involves a great number of small and medium enterprises, such as restoration companies, installation companies (e.g. lighting installation, conditioning and heating systems, air quality control), packaging and transportation companies, small and medium companies which produce technological instruments and measurement devices, and control and analysis equipment, test laboratories, producers and manufacturers of various materials: paints, stones, plastics, glass, paper, mortars, cement, wood composites, archaeological excavations companies or institutions, etc.

The development of standardised test and analysis methods will provide the cultural institutions, enterprises and laboratories with correct instruments for carrying out their work, improving, at the same time their proficiency / competencies.

The standardisation for the conservation of Cultural Heritage may influence, determining also specific requirements, the production and adjusting of the following kind of equipment, products and devices:

- Scientific equipment for laboratory and in situ chemical, geological, physical, mechanical and biological tests, measurements and analysis, in particular, for what concerns non-destructive ones, and production of standard reference materials whose compositions match those of cultural material (i.e. ancient alloys compositions), and reference data related to compounds found in degraded material for analysis purposes.
- Products used in the different steps of the conservation work / treatment, such as cleaning agents, biocides, sealing materials and mortar for restoration, surface protective materials, water- repellent materials environmental friendly, varnishes, glues.
- Equipment and technologies used during the conservation / restoration work (e.g. nebulizers / vaporisers, micro and macro-airbrasive machines, laser equipment), which are respectful of the professionals' health, of the cultural property and are environmental friendly.
- The materials / products, the equipment and technologies used nowadays in the conservation and restoration works, or which are used in diagnostics laboratories, are materials and equipment often produced by multinationals industries with great

experience, but these products and devices haven't been studied specifically for conservation or restoration purposes and, for this reason, need to be characterised and require a specific standardisation activity.

Finally, the programme of work of this CEN/TC, while defining the requirements and characteristics of the materials, of the equipment and technologies, can contribute to the improvement of the existing materials and equipment, and support the development of new ones for a more competitive European market.

3 Economical factors in relation to the objectives of CEN/TC 346

The increasing atmospheric pollution, of different origins, causes decay of exposed building surfaces and the identification of environmental parameters and assessment of material-environment interactions is a cost effective way to increase longevity and reduce maintenance costs [4].

The importance of using correct materials in conservation work is crucial, as experience has shown, for example, that poor quality natural stones used to repair historic structures have in some instances, deteriorated to such an extent that complete restoration has had to be undertaken, costing millions of Euro.

Safety is another element to be taken seriously, because wrong estimation of the durability of a product can lead to decay of some of the components, which in turn may lead to a fragile and possibly dangerous structure.

Standardisation in the field of conservation of Cultural Heritage will:

- improve the efficiency and pertinence of the diagnosis, reduce their costs , with a subsequent better management of funding for the conservation / restoration works and therefore increasing the number of conservation projects and spin-off economic benefits / opportunities for new investment, and consequent job creation;
- give precise and appropriate indication on the kind of diagnostics studies to be performed, avoiding expensive researches, promoting in this way conservation works on an increasing number of artefacts;
- help to develop and improve products, materials, equipment and technologies to be specifically used for the conservation of Cultural Heritage;
- increase the durability of conservation works therefore reducing costs on a long-term range because conservation operations will be spaced out.

To explain better the advantage of a good standardisation in the field of Cultural Heritage we report an example of a Venetian monument which was restored in 1976 as it was strongly decayed. The Porta della Carta, built in XIV century as the entrance door of Ducal Palace, was preserved in a rather good condition for four centuries and the only damage observed were ascribed to the natural weathering agents, as it is clearly visible in the photographic documentation of the last decades of XIX century (figs. 1, 2). Comparison between two pictures taken at the beginning of XIX century and after seventy years respectively (figs. 2, 3), shows a sharp increase in the marble decay, ascribed to the contemporary pollution increase occurring in the Venetian district as a result of the industrialization of Porto Marghera, the industrial area, created at the beginning of 1930's [5, 6].

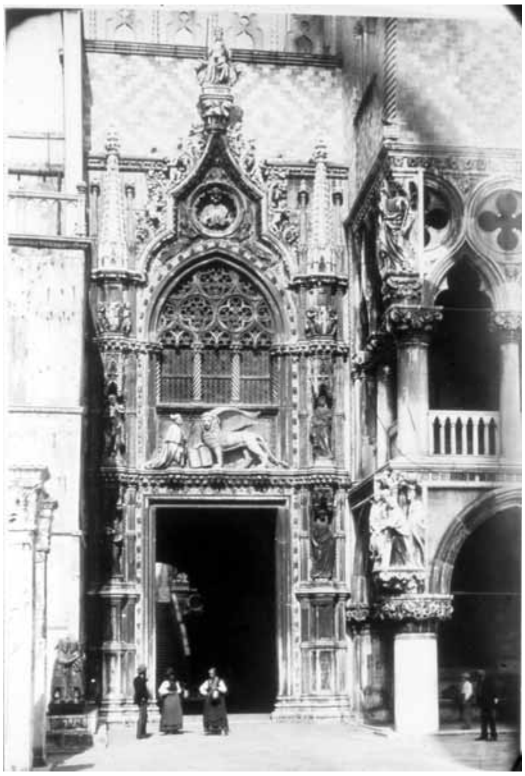

Figure 1: Porta della Carta in 1875

Figure 2: Temperance statue, Carrara marble, in 1900. The state of conservation was good

Figure 3: Temperance statue, missing parts are present due to marble disintegration, in 1976

The sharp decay observed in 60'ies induced people in charged in the conservation to recover inside the Ducal Palace museum the four statues to prevent their complete destruction. In 1976 the conservation work of the whole Porta della Carta started, thanks to a financing of the Venice in Peril fund, and it was completed in a three year period. In 2001 in the framework of the National Research Council Project finalized to the Safeguard of Italian Cultural Heritage in cooperation with the Venice Superintendence for Monuments Care a check of the durability of restoration materials used in 1976 restoration work and of the state of conservation was carried out. The results obtained allow us to conclude that the decay processes, which caused missing of pieces of marbles and disintegration of carved surfaces (as it is possible to observe from the comparison of figs. 2 and 3), since the beginning of industrialization until 1976, seems to be arrested or slowed down as it is possible to observe from the comparison of figs. 3 and 4 [7].

We can conclude that the stone treatment is still working after 25 years from the restoration work [8]. We believe that standardization in the field of Cultural Heritage will help to develop and improve products and technology increasing the durability of conservation works therefore reducing costs on a long-term range because conservation operations will be spaced out.

There are also a number of national research programmes funded by EU member states for Cultural Heritage studies. Italy, for example, has allocated a budget of € 40 million over five years (1997-2002) for a special project on the safeguard of Cultural Heritage.

Let me make some other examples: for instances Sweden provides research grants through its Central Board of National Antiquities; the Netherlands announced that cultural heritage will be one of ten research themes for funding by its Organisation for Scientific Research (NWO) over the last three years; the Spanish Ministry of Science and Technology provides funds under the category Civil Construction and Conservation and Restoration of Cultural Heritage and the UK government funds conservation work undertaken by English Heritage, Historic Scotland and the National Trust.

Figure 4: Temperance statue in 2004, after 25 years from the restoration

Figure 5: Porta della Carta in 2004, after 25 years from the restoration

The need to identify environmental parameters and assess material-environment interactions are also extremely important considerations to be taken into account in permanent presentation conditions in museums, galleries, libraries and archives, in temporary exhibit galleries, in stores and in transport packaging of works of art.

4 Social factors in relation to the objectives of CEN/TC 346

The most obvious aim is to preserve the European Cultural Heritage and the conservation of the cultural roots is an essential feature of the European society that is establishing a union of peoples rooted on the best of the culture of each country [9, 10].

Works of art are the most appreciated aspect of each people, easily understandable and free from political conditioning: the most attractive way to establish new links between peoples, thanks to pleasant tourism and cultural appreciation. Culture and works of art constitute an extremely powerful spring that moves mass tourism and reinforces the economy, establishes business, with the perspective of developing new employment. Again, it is also obvious that modern society cannot look to the future while loosing its past [11, 12].

We are now recognising the role of Cultural Heritage in enriching the quality of life, giving answers to questions about our historical origins, economic and political drivers.

This constitutes a key effort to improve the conservation of European Cultural Heritage.

5 Users of CEN/TC 346

Users of the standards developed by CEN/TC 346 are:

- Public and government bodies (e.g. Ministry of Culture and Education, Government Agencies);
- Public national and international non-government bodies (e.g. ICCROM, ICOMOS, IIC, ICOM, Regional administrations, Provincial administrations or local governments);
- Restoration / Conservation schools;
- Ecclesiastical bodies / organisations;
- Public and private analysis laboratories;
- Restoration companies;
- Professionals in the field of conservation and exhibitions planning;
- Distributors and manufacturers of materials used in restoration;
- Companies specialising in the preparation and organisation of exhibitions;
- Transportation and packaging companies;
- Lighting installation companies, air conditioning and heating installation companies, informatics and advanced technology companies;
- Cultural institutions: museums, galleries, libraries, archives;
- Architecture and surveyors;
- Archaeological excavations companies or institutions.

A close co-operation should be established with European and International non governmental professional organisations dedicated to the conservation of cultural heritage, such as International Council on Monuments and Sites (ICOMOS), International Council of Museums (ICOM) or International Centre for the Study of the Preservation and Restoration of Cultural Property (ICCROM); the International Institute for Conservation of Historic and Artistic Works (IIC); the European Confederation of Conservator-Restorers' Organisations (E.C.C.O.).

6 Objectives of the CEN/TC 346

The main objective of CEN/TC 346 is drafting of European standards on well-experimented test and analyses methods, both in laboratory and in situ which will help conservation professionals in their restoration and conservation work, ensuring at the same time the possibility for European experts to exchange information on test and analyses methods on Cultural Heritage.

Therefore, this standardisation activity will permit to harmonise and unify methodologies for all the European area.

Identification of existing national standards and other documents will be the basis for the development of any European standard in the conservation of cultural heritage. Moreover, a parallel study to identify national Regulations shall be undertaken to identify the potential for national variation likely to interfere with the CEN/TC 346 activity.

Under the responsibility of CEN/TC 346, several Working Groups were established and these groups comprise experts from CEN different Member States for a co-ordinated European perspective. Existing National standards can be taken into account as basis for the development of European standards, and the final results will be the production of “EN standards”.

Based on the considerations above, the CEN/TC 346 proposes the following objectives:

- Terminology;
- Characterisation of the materials;
- Evaluation of state of conservation of the materials;
- Evaluation of the performance of the products to be used in the conservation work, including long-range stability;
- Evaluation of the performance of the methodologies for the conservation work, including long-range stability;
- Evaluation of outdoor and indoor environmental parameters/conditions;
- Evaluation of cultural property / environment interrelation;
- Transportation and packaging of the works of art.

7 Structure of CEN/TC 346 and Work Programme Chairman Mr. Vasco Fassina (Italy)

The structure of CEN/TC 346 is constituted by 5 Working Groups (WG’s), corresponding to the different main areas for which technical development work has to be done. Under each WG the standardisation projects, called Work Items (WI’s) will be developed.

7.1 CEN/TC 346/WG 1 – General guidelines and terminology Convenor: Mr. Lorenzo Appolonia (Italy)

This WG has the responsibility for the drafting of:
guidelines on conservation planning, including monitoring;
standards on terminology dealing with movable and immovable components, with degradation processes and its graphic and symbolic documentation;
guidelines on security and safety conditions relating to the use of cultural heritage by the public.

WI 001 Cultural heritage – Terminology
This standard has the scope of creating a common terminology as regards to movable and immovable cultural property, and the conservation of the cultural property and of the material constituting the cultural property themselves.

WI 002 Cultural heritage – Guide to the principles of conservation
This standard has the scope of establishing the different steps necessary to the knowledge of the cultural property, the deterioration processes, and the preservation work.

WI 003 Cultural heritage – Condition report of the cultural property
This standard has the scope of establishing a standard methodology to visually describe the state of conservation of the cultural property.

WI 004 Cultural heritage – Security of cultural property and safety of the public
This standard has the scope of establishing the condition of security for the public visiting the cultural heritage in historical buildings.

7.2 CEN/TC 346/WG 2 – Materials constituting cultural property Mrs. Vasilike Argyropoulos (Greece)

This WG has the responsibility to define tests and analyses methods:

- for the characterization of the materials
- for the evaluation of the state of conservation / preservation of materials

WI 005 Cultural heritage – Diagnosis on buildings surfaces and structures
This standard has the scope of establishing analytical procedures for the characterisation of the cultural property and of their state of conservation with regards to outdoor and indoor environmental parameters.

WI 006 Cultural heritage – Characterization and classification of paint and paintings
This standard has the scope of establishing analytical procedures for the characterisation of cultural property and of their state of conservation/preservation with respect to outdoor and indoor environmental parameters (last proposal under discussion in WG2).

WI 007 Cultural heritage – Characterisation of the state of conservation/preservation of cultural property
This standard has the scope of establishing analytical procedures for the chemical-physical (mineralogical if applicable) characterization regarding the condition of cultural property according to the different categories of materials to be defined (last proposal under discussion in WG2).

WI 008 Cultural heritage – Characterisation of stone and related building materials
This standard has the scope of establishing the analytical procedure for the identification of stone or related building materials according to the sub working items ((last proposal under discussion in WG2): -lime mortars, hydraulic mortars traditionally used in historical buildings.

7.3 CEN/TC 346/WG 3 – Evaluation of methods and products for conservation works Convenor: Mr. Vasco Fassina (Italy)

This WG has the responsibility of drafting documents on criteria to select methods and/or products and operating / working conditions in relation to the conservation/restoration, repair, maintenance and preventive conservation works; and of drafting documents on the evaluation of the methodologies to be used.

WI 009 Cultural heritage – Surface protection for porous inorganic materials – Evaluation of methods and products
This document has the scope of giving guidelines on test method and methods of analysis (in laboratory and in-situ) for the evaluation of the performance of the products and of the methodologies to be used in protection of cultural property.

WI 010 Cultural heritage – Consolidation products – Evaluation of methods and products
This document has the scope of giving guidelines on test method and methods of analysis (in laboratory and in-situ) for the evaluation of the performance of the products and of the methodologies to be used in consolidation of cultural property.

WI 011 Cultural heritage – Cleaning products – Evaluation of methods and products
This document has the scope of giving guidelines on test method and methods of analysis (in laboratory and in-situ) for the evaluation of the performance of the products and of the methodologies to be used in cleaning of cultural property.

WI 011 bis Cultural heritage – Chemical control of bio deterioration – Evaluation of methods and products (Proposed by ITALY and to be confirmed by WG3)
This document has the scope of giving guidelines on test methods and methods of analysis (in laboratory and in-situ) for the evaluation of the performance of biocides used against bio deterioration on stone.

WI12 Cultural heritage – Conservation of archaeological remains / objects – Evaluation of methods and products
This document has the scope of establishing the different steps necessary to the knowledge of cultural property, the deterioration processes, and the conservation procedures of archaeological remains (new proposal from DK on scope).

7.4 CEN/TC 346/WG 4 – Environment
Convenor: Mr. Jesper Stub Johnsen (Denmark)

It has the responsibility for the drafting of guidelines for the control of environmental variables, and of standards on the measurement of indoor, including exhibition and storage conditions, and outdoor environmental conditions, and on cultural property / environment interaction.

WI 013 Cultural heritage – Specifications on environmental conditions
This standard has the scope of furnishing a guideline for the choice and the control of the environment finalised to the conservation of indoor Cultural Heritage e.g. museums, galleries, archives, libraries, churches and historical buildings.

WI 014 Cultural heritage – Guidelines on the measurement of environmental parameters
This standard has the scope of furnishing a guideline for the measurements of environmental parameters finalised to the conservation of indoor and outdoor Cultural Heritage environment.

7.5 CEN/TC 346/WG 5 – Transportation and packaging method
Convenor: Mrs. Anne de Wallens (France)

This WG has the responsibility for the drafting of standards on methods of packaging and transportation of cultural heritage outside the institutions.

WI 015 Cultural heritage – Principles of transportation and packaging of cultural property
This standard has the scope of giving a guideline for the choice and the control of the microclimate finalised to the transportation and packaging of cultural property.

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Database management and innovative applications for imaging within museum laboratories

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Key words: digital imaging, databases, content management, visualization

Abstract
In this paper, we give an overview of the many EU projects that the C2RMF has participated in. These have been in a wide range of fields such as digital imaging, 3D modelling, ontologies, content-based retrieval, visualization and database management. We will highlight the key achievements of these projects, how various technologies have evolved across projects and how we have tried to bring these different strands together.

1 Introduction

The *Centre de Recherche et de Restauration des Musées de France* (C2RMF) was created in 1931 with a mission to study, catalogue and help preserve works of art kept within all of the museums of France. The main laboratory is housed within the Louvre Museum in Paris with a smaller laboratory within the grounds of the Palace of Versailles. The laboratory performs not only restoration, but scientific studies, especially chemical and materials analysis, imaging (X-ray, infra-red, multi-spectral etc) and even has a particle accelerator.

The C2RMF has been an active participant in a total of 11 EU projects (within the ESPRIT, IMPACT, RAPHAEL, IST and e-CULTURE frameworks) since 1989. These projects have helped transform the way the C2RMF gathers, handles and uses its digital data. These projects have involved a wide range of topics, encompassing many aspects of the work carried out in the Centre. Many projects have also tried to build on and extend the work carried out in previous projects, resulting in a coherent and inter-dependent body of work.

2 Digital imaging

2.1 Digital scans

The creation of the first digital image archive at the C2RMF was made possible by the NARCISSE EU project in 1989 in which historic scientific photographic films were scanned using a high resolution (6,000 × 8,000 pixels) scanner [Figure 1].

2.2 Direct digitization

Direct colorimetric digital capture was the logical next step and has been an key aim of several projects. The VASARI project created the first multi-spectral camera system for museums. This consisted of a seven filter camera which took a mosaic of images at visible wavelengths between 400 nm and 750 nm resulting in a final image of 10,000 × 10,000 pixels. To prevent the painting from being damaged by the intense lighting normally required, the filters are used to filter the light incident onto the painting, rather than being used to filter the light reflected into the lens as is more usually the case. Colour accuracy was also a key objective. By using colour reference charts in conjunction with the 7 filters, extremely accurate colour reproduction is possible of the order of 1ΔE in the CIEL*a*b* colour space. Advanced image processing software was developed [1] to handle these large images with limited amounts of memory using partial input / output based methods. The software performs post-processing operations, such as noise reduction, gain calibration, lighting normalization and colour processing.

Figure 1: Thomson Scanner

Figure 2: CRISATEL multi-spectral camera

The VASARI camera system, however, was not portable and somewhat cumbersome. The later CRISATEL [2] project, therefore, was put together to take these principles further and create a system that was portable, easier to use and also accurate enough to perform spectral reconstruction. Instead of an image mosaic, this camera consists of a CCD linear array of

12,000 square pixels (6.5 µm × 6.5 µm each) synchronised with a scanning linear beam lighting system. This novel lighting design is a different way of solving the problem of light damage on the painting. The filters in this case are in front of the lens as is normally the case, but only a thin strip of the painting is illuminated at any one time. The light source sweeps across the painting in synchronization with the CCD array resulting in an image of up to 12,000 × 20,000 pixels. A resolution of 100 dots per millimetre can be obtained on small painting or on small areas of interest. In order to perform spectral reconstruction, 13 interferential dichroic filters in total are used covering the spectrum between 400 nm and 1000 nm. Within the ultra-violet and visible part of the spectrum these each have a bandwidth of 40 nanometers and within the infra-red a bandwidth of 100 nanometers. These systems have been used to scan paintings in several French museums (including works by Renoir and the Mona Lisa) in unprecedented accuracy and resolution.

3 3D imaging

3.1 Panoramic imaging

The ACOHIR project took the concept of high resolution colorimetric digital imaging into the realm of 3D objects using a turntable to take a photographic panorama of the object. A small object is placed on the computer-controlled turntable and a number of views (24 or 36) taken with a high-end digital camera at equal angles. These images are colour calibrated via a colour chart using software based on that developed during the VASARI project. The result is a colour accurate image sequence that allows the user to navigate around the object see details that would be impossible to see in a museum.

Figure 3: ACOHIR turntable and lighting

3.2 3D Modelling

This idea was taken a step further with the SCULPTEUR project. In this project, the same apparatus was used, but with a geometric reference target as well as a colour target. The silhouette is subtracted from each image and then the results volumetrically mapped into 3D models by means of silhouette extrusion [3] [Figure 4]. The visual hull is an upper-bound of the real object volume and corresponds to the intersection of all the silhouette cones.

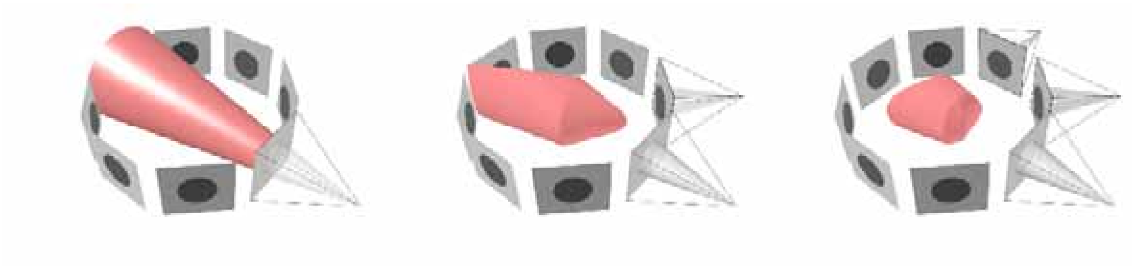

Figure 4: Volume carving by silhouette extrusion – visual hull

For each image, the apex of the silhouette cone is the position of the camera and the corresponding silhouette in the image plane defines the generator of the cone. The visual hull is then carved in order to recover the missing concavities of the object surface. The core of the method is based on a deformable model which is driven by the attraction of two external forces based on the images: the texture and the silhouettes. These two forces are complementary; the silhouette driven force aims to keep constant the visual hull of the model during its deformation and the texture force to carve the model in order to approach the real surface onto which high multi-stereo correlation has been obtained. At the end of this iterative process we are able to recover the computed contours of the model. A colour calibrated texture map is derived from the original images for the reconstructed 3D model. This method, although labour-intensive, results in highly detailed models [Figure 5]. Several hundred objects from the Louvre, the Musée d'Orsay and several regional museums have been digitized in this way.

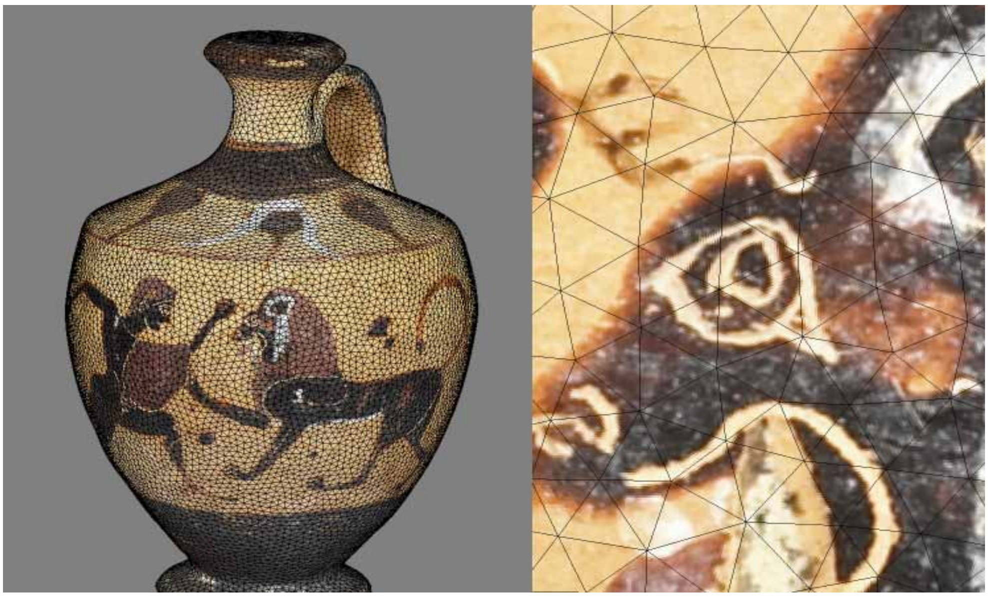

Figure 5: Reconstructed 3D model overview and high definition detail

4 Visualization

High resolution colorimetric images such as those produced by the VASARI camera require special software to visualize efficiently. The VISEUM project was instigated to develop a means of efficient remote viewing to allow images to be shared not only within institutions, but also between different institutions over the internet. The system designed was a client / server architecture based on tiled multi-resolution images [4]. The client requests a view of the painting at a particular resolution and the server extracts the tiles corresponding to that view at the appropriate resolution. This not only minimizes the load on the server, but also minimizes the bandwidth necessary, as all that is sent is data corresponding to the size of the view-port of the client. In this way, very high resolution images that would be impossible to manipulate on a local machine can be easily viewed remotely with minimal system requirements.

This software was also extended to visualize the panoramic images of objects produced as part of the afore-mentioned ACOHIR project.

5 Content based retreival

The automatic analysis of these high quality images by the use of content-based retrieval techniques was carried out in the ARTISTE project. Each image is classified according to various features such as colour balance, colour coherence or the spatial distribution of luminance etc. For each criteria a similarity vector is determined, which can be used to measure the similarity between two images. By performing this comparison for each criteria on every image, it is possible to find related images. This technique was extended to 3D models in the SCULPTEUR project, where various shape criteria were analysed for each 3D model.

6 Content management

6.1 Technical vocabulary

This NARCISSE project, which started the digitization programme also allowed the C2RMF to set up its first database on their works of art, and the related scientific photographs and technical reports. To complement this effort, a later project, called CRISTAL, created clear definitions and translated much of the technical terminology and key-words used in the database into 10 languages, including not only European languages such as, for example, English, French, Italian, Greek, Estonian, Finish and Georgian, but also into Chinese, Japanese and Russian.

6.2 Ontologies and semantic mapping

The use of dictionaries and controlled terminologies poses problems when attempting to compare different databases, especially those in different languages. In order to solve this problem, ontologies are required to map the relations between concepts and meanings. Part of the SCULPTEUR project was to map the database structures in use at the C2RMF to the ICOM-CIDOC standardized relational mapping, thereby allowing any two databases with a CIDOC mapping to be mutually compatible. The use of this semantic mapping is vital in order to enable deeper international cooperation between research centres.

6.3 Database management

The large quantities of data produced by the digitization of images and documents have required careful management. The C2RMF currently has several terabytes of data online on dedicated servers. The NARCISSE project started this process, but a more advanced database was soon required. Several projects partially addressed some of these issues, which led the C2RMF to develop the custom open source EROS database system [5] targeted at conservation-restoration for research applications. The aim of this was to allow the disparate results of the various projects undertaken to be brought together and exploited in a unified and coherent way. The system brings together the initial data created in NARCISSE and adds the translations undertaken in CRISTAL to the semantic mapping to give a dynamic multilingual access to the contents of the database in 10 languages. Furthermore, the remote viewing system from the VISUEM project was integrated to enable access to the high resolution multi-spectral images, 3D panoramas and reconstructed 3D models.

7 Conclusion

7.1 International impact

These projects have opened up collaboration between the C2RMF and many other European museums, including the National Gallery in London and the Uffizi in Florence as well as several universities and research institutes, such as the University of Southampton, the Ecole Nationale Supérieure des Télécommunications, Paris and the French CNRS computer science research laboratories. These partnerships have endured after the end of their respective projects and have continued both within follow-on projects and on an informal basis.

Furthermore, areas of study, such as the focus on multilingual access, semantic mark-up and ontologies has allowed the C2RMF share its data internationally with other interested museums and research centres. This has resulted in the forging of links with European-based institutions in Estonia, Finland and Greece outside the scope of official EU projects.

7.2 Innovation and originality

Many of these projects have been at the cutting edge of technology and their application to cultural heritage. The leading of these are perhaps the two digital multi-spectral imaging projects – VASARI and CRISATEL. In terms of both hardware and software, these projects pushed the boundaries of high resolution digital imaging and are references in the world of multi-spectral imaging. In addition, the image processing and visualization software developed go have capabilities beyond previously available systems. The remote viewing of very high resolution data with extended dynamic range (eg. 16 bit resolution) is unique to the IIPImage system.

The work on multilingual access and ontologies has allowed the C2RMF to dynamically translate the database contents into 10 languages. Databases have often had their user interfaces translated, but rarely the contents themselves in this way.

The ACOHIR and SCULPTEUR projects were highly advanced in terms of 3D modelling and have allowed us to build up an unrivalled collection of over a thousand high quality digital 3D models of museum objects.

7.3 Impacts

These projects have profoundly changed the way photography and technical reports are made, used and distributed within the C2RMF. The move to digital imaging has changed the role of photography and scientific imaging. Digital imaging is not only useful for qualitative viewing, but also for more quantitative analyses. Accurate and reliable measurement and recording of colours, spectra and the modelling of works of art has opened whole new fields of research for such applications as non-destructive pigment determination.

The availability of the data remotely has allowed a far larger diffusion and reuse of information by the C2RMF and other museums.

The software developed within several of these projects has continued to not only be used, but have found lives of their own after the end of the official projects. The advanced image processing system, VIPS [1], initially developed to handle the high resolution images of VASARI and the IIPImage remote viewing system [4], initially conceived for VISEUM have been released as open source software and are now often used within the digital imaging community and freely available on the internet.

8 European project details

VASARI	Visual Art System for Archiving and Retrieval of Image (ESPRIT II, 1989-1992)
NARCISSE	Network of Art Research Computer Image SystemS in Europe, (IMPACT 1, 1990-1994)
VISEUM	VIrtual MuSEUM International (ACTS #AC238, 1996-1998)
MENHIR	Multimedia European Network of High quality Image Registration (ESPRIT 4 #24378, 1997-1998)
ACOHIR	Accurate Colour High Resolution Recording and Reproduction of 3D objects (ESPRIT #23276, 1997-1999)
CRISTAL	(Raphaël 1999-2000)
ARTISTE	An Integrated Art Analysis and Navigation Environment (IST #11978, 2000-2002)
CRISATEL	Conservation Restauration Innovation Systems for Image capture and digital Archiving to enhance Training Education and lifelong Learning (IST #20163, 2001-2005)
CHERI	Cultural Heritage RIch media secure value chain (IST #28044, 2001-2002)
SCULPTEUR	Semantic and content-based multimedia exploitation for European benefit environment (IST #35372, 2002-2005)
e-Culture Net	European Digital Culture Research and Education Network (1999-2000)

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Fragmentary mural paintings – possibilities of aesthetic presentation and exemplary communication

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Key words: presentation of fragmentary mural paintings, semantic mapping, digital archives

1 Introduction

In order to maintain public interest in our material cultural heritage, appreciation of the material objects of the past must not be lost. That which is appreciated and thought to be of value will be conserved. But conservation measures are often controversial with the question at the centre of debate often being not whether, but rather how they are to be implemented. Should one conserve puristically and maintain only that which still exists? Or should one take a further step and display through restoration that which is almost entirely lost? The latter aims at restoring dignity to lost contents and at making them tangible for the viewer. This comes with certain dangers, since for the most part it is possible to choose only one of a number of very different alternatives. And once something has been done, it can rarely be undone. In the field of heritage conservation one often encounters fragmentary works of art which prove inaccessible to most viewers precisely because of their defects.

Generally speaking, there are grave deficits in the communication and public relations of restoration projects as well as in the communication of fragmentary art. Complex decisions for or against specific measures in particular are mostly made by a small circle of experts. The public – the actual addressee – is excluded as a rule; this is a mistake if one wishes to strengthen the general consciousness of the value of our material cultural heritage and the power of democratic decisions. At the very least, the viewing conventions and the stimulating psychological processes at work precisely in the perception of fragmentary and destroyed works of art should be taken seriously and the viewer should be allowed to take part in the intellectual game. For without active looking the trend towards indifference and ignorance will grow, which cannot be in the interest of a Europe defining itself not least by its cultural values.

This is exactly the problem presenting itself in Bamberg’s Dominican Church which features a complex inventory of superposed murals of high artistic quality. The individual and very different pictorial programmes from the early 14th to the closing 16th century can no longer be deciphered due to their fragmentary nature, especially as the contents are hardly anchored in contemporary consciousness. It was decided in 2004 to institute a research team of restorers, architects, scientists, computer scientists, and psychologists to solve the problem of how to deal with the chaos on the walls of the present university auditorium. The murals are to be taken seriously, their bizarre fragmentary nature is to be preserved, and at the same time the beholder is to be encouraged to look. This necessitated a new approach to research, which was to be “as-well-as” rather than “either-or”. Accordingly, the contents of the interdisciplinary project are very varied. The campaign began with a complementary art historical and art technological examination of a selected area of the murals. The paintings were documented using a novel mapping tool, the so-called Mobile Mapping System (MMS). The novelty lies in particular in the storage of content meta-data during manual mapping. Subsequently, the possible aesthetic interventions were simulated (and hotly debated) by means of a virtual discussion of alternatives prior to actual conservation and restoration. In parallel, the large amount of data already existing and still growing was and continues to be archived systematically. For this, digital software specialised in the space-oriented filing of information, the so-called Digital Monument Archive (DMA), is employed. The innovative feature of the system solution is the content-based (semantic) search functions which allow the comparison of documents, be they photographs, maps, constructional drawings, or the results of the MMS-mappings. A particular emphasis of the project is the communication of the contents of the many-layered medieval paintings which are difficult to grasp. For this purpose and for the first time ever the many and very differently educated visitors of the Dominican Church are interviewed with psychological assistance about their personal perception of the fragmentary chaos of paintings. Based on the newly compiled visitor profiles we attempt to inspire the viewer to navigate through the layers of murals and to deliver targeted information on the currently gained insights regarding the paintings. We are aiming at an exploration of the destroyed work of art which turns looking at the painting into an intellectual pleasure and which whets the appreciation for the conservation of our material cultural heritage.

2 The murals in the Dominican Church

The former Dominican Church [1] of St Christopher in Bamberg is among the outstanding late medieval buildings of Bamberg's UNESCO World Cultural Heritage Site (fig. 1). From the early fourteenth century until secularisation the Dominican mendicant order's monastery was an important centre of pastoral care and spirituality shaped by the Dominicans [2]. The Dominican Church, constructed in the early fourteenth and fifteenth centuries, possesses a rich inventory of murals and wall paint of the highest quality spanning five centuries.

Figure 1: The Dominican Church in Bamberg, (IABD 2005)

The tradition of filling the unadorned church building with individual panels of paintings bit by bit, practiced over centuries, has resulted in decorative walls which transformed the otherwise sparsely decorated church interior into a sumptuous Lord's house. The walls display sacral pictorial motifs, for example scenes according to contemporary perceptions from the life and ministry of Christ, of Saints of the church and of the people. Images of coats of arms placed below the paintings panels indicate that the paintings in the Dominican Church were donated by burghers to their salvation. The separate panels differ not only in their formats and in the technique of their execution, but can also be distinguished clearly by their individual pictorial styles. Due to changes in aesthetic tastes, but due also to reasons of space, newly added picture panels were painted over or into existing murals over time. This process led to a multi-layered inventory of several intricately overlapping planes of decoration from very different eras. In the Baroque, the decorated walls were whitewashed [3] and therefore fell into oblivion for a long time. Only in the early twentieth century were the murals rediscovered. Restorers began uncovering the picture panels. The measures were executed with coarse tools and without making allowances for or even recognising the complex and many-layered inventory. Extensive remainders of the whitewash prove that the exposure was not completed, that it may have even been abandoned, possibly due to the unattractive appearance. After World War II, the church interior was whitewashed several times; the uncovered areas were therefore largely spared further interference. The Otto-Friedrich University Bamberg has been the occupier of the Dominican Church since 2002. Initial restoration measures have allowed the use of the premises as the main lecture hall. Since then, university and cultural events, conferences and exhibitions have alternated in the Dominican

Church. Due to the varied utilisation of the former church and particularly due to the results of the research project and of the restoration, the murals are once more brought to public attention.

3 Problems of fragmentary murals

Figure 2: View of western wall, Dominican Church, Bamberg, (IABD 2002)

Figure 3: The fragmentary murals in the church (VITRA 2003)

An area of about 36 square metres on the western wall of the nave-aisle was selected for the research project. There, three fragmentarily preserved murals and remainders of coats of whitewash lie one over the other. The arbitrary uncovering and restoration of the 1930's, decades of neglect and harmful climatic influences have severely damaged the remaining murals and have led to enormous aesthetic interference.

At the moment the observer of the Dominican Church is presented with a barely comprehensible and most confusing sight of overlying layers of undercoats, paint, and whitewash. Their poor state of preservation means that they affect each others' perceptibility in a conglomerate of various fragments.

An immediate experience of the pictorial programmes' beauty as a major design feature of the Dominican church is rendered impossible or at least very limited for the visitor because of their restricted legibility. There are only few indicators which shed light on the subjects. Unlike in many churches, where the meaning of the paintings is immediately intelligible, the paintings in the Dominican church require lengthy contemplation in order to recognise a meaning; the aesthetic pleasure must be worked for hard. Elaborate commentary on the iconographic contents and the objects' history is necessary to motivate the viewer to engage with the heavily damaged artwork.

But the communication of the value of art is the immediate precondition for the long-term preservation of testimony of a past era. The first concern of a preservation concept for historic monuments is therefore, apart from asset conservation, an appealing presentation and communication of the works of art.

4 Interdisciplinary approach to research

The interdisciplinary research project merges the traditional examination methods of Building Archaeology, History of Art, and Conservation Sciences with novel instruments in informatics and psychology. The central concern of the research project *"The Mural Paintings of the Dominican Church in Bamberg, Bavaria – Exemplary Restoration, Conservation and Reconstruction of the Paintings by a selected Area"* is a comprehensive scientific survey of the murals and decoration phases of the selected area. A further focus of the research project is on the aesthetic treatment of the many-layered and fragmented works of art. The multitude of possible aesthetic interventions and their effects on the paintings' appearance are to be demonstrated and discussed with the help of virtual variants. A further area of research deals with the communication of the complex and difficult to understand temporal layers to the visitors of the Dominican Church. The goal is to afford the observer access to the murals. A concept is to be developed which encourages engagement with the works of art. In this, interdisciplinary work is the precondition for ensuring both the preservation of the murals as well as an appealing presentation. This particular problem requires a new scientific and comprehensive approach between restoration and science, which has been tackled since early 2005 by a team of restorers, scientists, computer scientists, psychologists, art historians, and architects.

5 Scientific inventory

The research into the Dominican Church's murals requires a circumspect treatment of various digital data formats produced over the course of work on the project. In this context, the task of collecting, orderly filing, and archiving such data presented itself in order to allow other researchers easy access to the compiled material in future. For this purpose two software components of a programme, the Digital Monument Archive and the Mobile Mapping System, were used which in combination form a novel documentation and information system already in use across Europe.

6 The Digital Monument Archive (DMA) as a tool of European importance for the archiving and analysis of building data

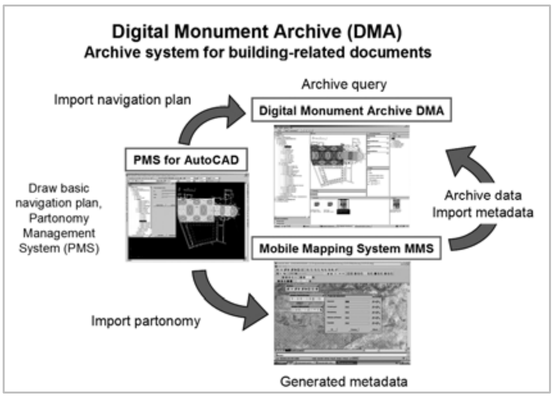

Figure 4: All components of the DMA

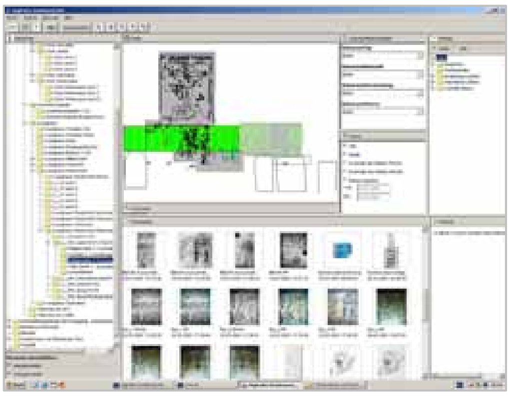

Figure 5: Surface of the Dominican Church in the DMA

The Digital Monument Archive was developed over the years 2003 and 2004 in a project entitled "Development and model application of a digital documentation system for the recording of environmental damage as part of a comprehensive care and prevention system for the cathedral church in Passau (Bavaria)" funded by the DBU (Deutsche Bundesstiftung Umwelt, German federal Environment Foundation). The system component Digital Monument Archive (DMA) was programmed by the University of Passau under the direction of Prof. Burkhard Freitag at the Institut für Informationssysteme (IFIS).

The DMA is a multifunctional documentation and information system which takes on the administration of building data and at the same time possesses analytical functions. Methodically, historical and current data of widely diverse contents and formats such as accrued in the course of the complex art historical and restoration survey process in the Dominican Church – photographs, text, digital and analogue constructional drawings, tables – are to be processed and evaluated using a single digital platform. Parts of the software were to be a central archiving solution with data access modelled on the building and a mapping tool (MMS) based on mobile terminals (fig. 4).

The main concern of development was the installation of an archiving solution with intelligent navigation for digital documents to be stored for a long time. This requires of the software the simple finding of documents and the possibility of updating data by chronologically filing processed versions (data history).

The DMA allows the modelling of individual systems of classification. This has the advantage that historic buildings for which documentation does not yet exist can be assigned a simple space-related reference system, too. The simplest solution offers itself in the form of a description of the building's hierarchical structure in its separate parts, which corresponds to the established PC folder structure and which is designated a partonomy in computer science. For the first time, an archiving solution permitted the filing and processing of data orientated on the building. The software allows tow kinds of navigation: on the one hand, in the freely definable hierarchical order of the respective monument, which one installs oneself by way of the conventional tree-structure, and on the other hand via the building's plan. The rapid and targeted access to information and the navigation within the archive is effected through a graphic user interface (fig. 5). The targeted query of documents relevant to the building can be retrieved via the very comfortable graphic interface in the form of a building plan by clicking on the floor plan or the elevation of the respective building part or the linked area of the mural. Thus, the data are accessible from documentation and allow differentiation into the smallest chosen unit (e.g. 1st period of painting, single stone). The comparative evaluation and visualisation of photographical and cartographical data supports the prediction of damage progression in the mural and project planning as well as enduring preservation in future. Comparative analysis and knowledge-based evaluation is to be made possible by linking the data.

Documents to be archived can be specifically assigned to building parts and provided with metadata, i.e. background and file information. The transfer of data from existing ones takes place by means of the "drag&drop" function: in doing so, the associated metadata are included automatically and can be amended if need be. Additionally, the DMA includes content-based (semantic) search functions.

Since the existing architecture elements provide access to the digital information, the system solution possesses normative character: disputes over nomenclature arising from different building typologies or terminologies are overcome by the language of drawing. The newly developed programme is not only of European, but also of interdisciplinary importance. The application of the DMA can be extended to other subject areas; thus it can also be applied in an urban planning context or in the documentation of archaeological finds. Language masks allow easy adaptation to the respective languages in use. The Digital Monument Archive is recommended [4] for the use as archiving tool for all site offices by the European Dombaumeistervereinigung (association of cathedral restorers) and is currently being applied; thus, it could become a platform for a large circle of users, thus building bridges throughout our polyglot Europe.

7 The Mobile Mapping System (MMS)

Prior to the conservation and restoration campaign, the murals in the Dominican Church were recorded in an elaborate cartographical documentation with the aid of a novel cartography software, the Mobile Mapping System (MMS). The CAD-based Mobile Mapping System was developed as a software for the recording and documentation of historic buildings under the direction of Prof. Christoph Schlieder of Bamberg University's Chair for Computing in the Cultural Sciences [5]. It is a tool with which inventory, damage, and task mappings can be conducted with the help of mobile terminals (e.g. tablet PC) directly on the scaffolding. The documentation operations were based on a high-resolution photographic image which was generated on the course of the VITRA project in 2003 [6].

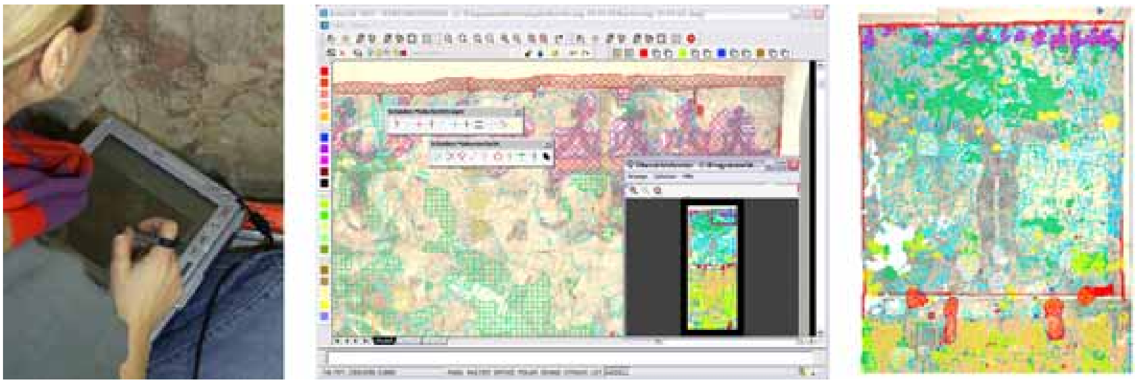

Figure 6: Mapping with the Mobile Mapping System (Fundel 2005)

The complexity of the many-layered store of murals and the multitude of widely different damage phenomena necessitated an adaptable mapping systematics in the first place. Since there is no authoritative standard of terminology in the area of restoration, flexibility is the most important requirement of the MMS's mapping system. It is assured by means of attaching any factual data (semantic mapping) to maps, of individual modelling of the technical terminology and labelling systems (mapping glossaries and spatial frames of reference) as well as of self-referential description of digital maps (generation of metadata in a database deposited). The conversion of a technical terminology by way of a glossary in the MMS greatly simplified the acquisition of factual data. Also, conceptual super- and subordination, so-called taxonomies, within a technical terminology can be represented and put to use in evaluation. Expressed in the language of computer science, the user gains the possibility of object-oriented data modelling. This is an innovation not only in the area of mapping software used in the preservation of historic buildings, but is also unknown in this form in standard CAD software. For the user, this means above all the simplification of data input and an almost limitless adaptability to respective requirements. In this context, too, it was kept in mind to keep the adaptation effort as low as possible.

The MMS documentation tool supports the semantic search within the DMA. Not least, it also profits the search for digital maps in the archiving system, as the latter allows the user to employ the glossaries and their concepts respectively in the phrasing of queries. Further adaptation of the MMS to the users' requirements is accomplished for example by the specification of icons for the mapping and compilation of frequently needed drawing commands in toolboxes. This software combination is therefore a fully-fledged documentation and archiving solution with the option for the integral search for space-related data. The digital mapping of the murals in the Dominican Church was based on a glossary determined in advance by restorers which comprised inventory, damages, and measures conducted. With the aid of the MMS, the separate phases of painting, art technological phenomena, and different materials of the mural inventory can be recorded graphically and topologically, i.e. it was possible to link further commentary, descriptions, and information were with the geometries using the Database. Thus, the MMS prompts the user to enter particulars, e.g. on the degree of damage, via an input mask after having drawn a phenomenon. The user can select the particulars from pre-existing answers or phrase them himself. During the mapping of the current state, damage was registered and provided with comments on damage type, degree, and treatment. The records of the inventory and its current state were saved in a common file, so that complex correlations between material, phenomenon, and causes of damage can be clearly displayed. Data sheets, further information and in-detail records of certain layers of paint or damage phenomena were also able to be linked to the mappings. Thus, the restoration scientists have at their disposal an unusually densely packed information platform on the murals. The generated plans served as a graphic guideline for the practical conservation and restoration works on the wall. By now, the software is being put to use in several European countries [7].

8 Psychology and fragmentary art

The formerly sacral building of the Dominican Church today serves as a cultural venue at the heart of the Bamberg Cultural Heritage Site, which attracts audiences of very different horizons of knowledge and experience with its various events. The experience and perception of the cultural asset are fundamentally hampered by the murals' fragmentary state of conservation; the visitor's individual access to the work of art and therefore to appreciation is very much restricted. The visitor feels overtaxed. In the restoration treatment of fragmentary art, psychological insights regarding aesthetic perception are barely if at all taken into account. In his treatment of surface defects, Cesare Brandi refers to the rule-conforming nature of Gestalt psychology in his Teoria del Restauro, published in 1950, but the great majority of psychological processes in a person, that is the viewer, involved in aesthetic sensation, remain unheeded [8]. It is the goal of the psychological approach to our research to allow all visitors, expert as well as lay, to access the damaged paintings. Historic-iconographic contents and restoration findings were prepared and communicated in such a manner as to motivate the observer to engage with them. At the moment, this is achieved by means of guided tour attended to by art historians directly at the wall as well as informative posters with background information. The execution of the restoration measures the retouching, also serves the improved optical perception of the wall's subjects. It will be necessary, however, to go way beyond these established methods.

To this purpose, there is a close co-operation with the Institute for Theoretical Psychology at Bamberg University. It needs to be investigated in co-operation with the restoration scientists which cognitive processes (perception, thought, emotion) are determining in encouraging the viewer to engage with the art of a bygone era and its world-view and thereby in achieving a positive experience of grown history. The psychological processes (motivation, cognition, emotion) involved in the perception of fragmentary art are being investigated for the first time by the Institute for Theoretical Psychology based on model considerations. The psychologists that man – and aesthetic sensation as an important attribute of human existence – must be considered holistically. Emotion does not occur independently of motivation and cognition. At the Institute of Theoretic Psychology, the interplay of the different mental instances is explained and investigated by a theory – the PSI-theory according to Dietrich Dörner [9].

Dörner relates aesthetic perception to the complicated interplay of reduction and multiplication of uncertainty (certainty is an innate need according to his theory). The reduction of uncertainty is experienced as "pleasurable", since a need is gratified. Should the environment not afford the possibility of reducing uncertainty (as, for example, a very well known environment), an important source of pleasure is lacking. In such cases, uncertainty must be actively sought out (diversive exploration), which can then be reduced (specific exploration) in order to experience pleasure and retain a high level of competency. Art in all its forms principally serves this need: the experience of uncertainty and the reduction of uncertainty. The interplay of searching for certainty and uncertainty is explicitly generated by the need for certainty and the desire for competency [10]. Based on these considerations, the following hypotheses can be advanced:

- That aesthetic sensation is shaped by the alternating search for and reduction of uncertainty;
- There exists a learning process: the more experience one has in the reduction of uncertainty, the better able one will be to reduce more complex indeterminacies as well;
- The sensation of beauty depends on the experience of pleasure and therefore on the degree of competency additionally gained.

First psychological surveys of students confronted with the murals' chaos seem to confirm the hypotheses specified above. The theory is evidently capable of explaining and predicting complex behaviour and its effects on cognition, emotion, and motivation [11]. Furthermore, it is to be investigated to which processes of information processing aesthetic sensation can be ascribed.

9 Variant discussion of the restoration intervention

Through conservation and restoration, the overall effect of a work of art is fundamentally altered, for the desire for an improvement of aesthetic appearance is associated with every intervention. The measures are contingent on personal opinions and current tastes and fundamentally alter the perception of a painting. Today, restoration is undertaken on the based of the artistic and historic statement of the work of art interpreted as source. It is attempted to satisfy both the authenticity and the artistic quality at the same time (bipolarity). Therefore, the restorer must in practice position himself between these two poles: but in the case of fragmentary works of art a certain degree of reconstructive interventions must always be considered. Virtual reconstructions and retouching can be employed to hypothetically demonstrate that which is to be shown, and also to plan the actual intervention. However, until now this possibility was not considered, not least because every discussion presupposes a prior survey which costs money. Nevertheless, the virtual play with the possibilities seems to us to be a precondition for a responsible treatment of our material cultural heritage for which money is well spent.

The aesthetic treatment of the painting panels in the Dominican Church is a particular challenge. They differ not only in the technique of their execution and in their individual pictorial styles, but they also exhibit various states of conservation. Purist solutions considering the historical background with all alterations involving no or minimal aesthetic interventions are as conceivable as are solutions which intervene more deeply in favour of legibility, for example by emphasising a single phase of painting. In the course of the research project, recommendations for the treatment and presentation of the complex painting programmes were developed. The simulation of retouching decisively influenced the actual restoration intervention in the object. In actual fact, by overlaying the inventory mapping and the MMS-mapping, the phases of painting were separated. With the aid of image editing software (Photoshop) the treatment and retouching possibilities were simulated and discussed in the project team's plenum (fig. 7). A determined and selected form of retouching and a degree of restoration visualised and discussed previously in virtual simulations served as the guiding basis for the restorers on site. The surface defects of the murals were optically contracted by low-key retouching, so that the observer can more easily perceive a totality of figures and contents by the colour values. Thus, virtual models within which the possibilities and effects of restoration interventions in the entire inventory were simulated can be important aids to the development of a holistic approach to the aesthetic presentation of the mural without having to interfere with the actual inventory. With the alternative possibility of rendering the murals more comprehensible for visitors through virtual models at hand, heavily interfering levels of retouching and reconstruction could at the same time be avoided. With merely a few perception aids at the object and by virtual simulation, the observer can now identify structures better, the complex stock is rendered more comprehensible, and orientation is facilitated. Thus, the appreciation of fragmentary art as a whole could be noticeably improved.

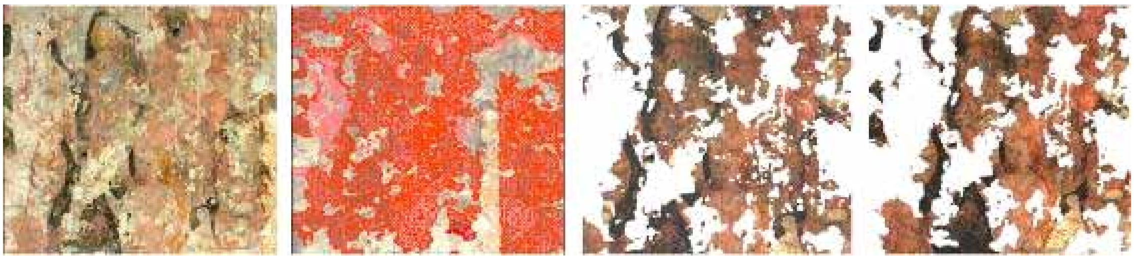

Figure 7: Process of virtually separating and retouching a phase of painting (Fundel, 2005)

10 Summary and innovation criteria

In the interdisciplinary research project "The Mural Paintings of the Dominican Church in Bamberg, Bavaria – Exemplary Restoration, Conservation and Reconstruction of the Paintings by a selected Area" a digital dual-component tool [12] was employed which is suitable for Europe-wide application due to its flexibility and its intelligent data management for objects of artistic and cultural value. All accruing data of survey, conservation and restoration of the murals in Bamberg's Dominican Church are systematically archived with the aid of the Digital Monument Archive DMA. A broad variety of data formats can be specifically and rapidly retrieved if the need arises. The mapping of the murals with the Mobile Mapping System MMS provides a documentation densely packed with information of both the state of preservation and the measures implemented.

Based on the MMS inventory mapping we can display the individual phases of painting separately. With the separation of individual phases of painting the effects of possible aesthetic interventions on the murals' appearance can be simulated in a virtual variant discussion in a subsequent stage. The intervention into the object can be concretely planned at the PC in the run-up already. On the one hand, this serves restoration scientists as an instrument in the planning of a restoration. On the other, the separation serves as an important aid for the comprehension and elucidation of the complex inventory of paintings for visitors to the Dominican Church. The decision for a particular restoration variant becomes universally comprehensible. This represents an entirely novel solution for the difficult restoration of fragmentary art. Thus, the virtual variant discussion serves as an aid for planning of and decisions on the restoration of fragmentary works of art. The public is informed about and sensitised to conservation and restoration measures. First results of the psychological analyses provide detailed insight into the mental processes involved in the perception and communication of the murals in the Dominican Church for the first time. Based on these analyses, visitor profiles are compiled. The restoration scientists compose and present information specifically aimed at the profiles. This interdisciplinary approach allows a holistic illumination of a destroyed work of art for the first time, which represents a novel and exemplary approach to the treatment of badly conserved works of art. It needs to be discussed on a European level and to be made transferable to other types of fragmentary art.

11 Acknowledgments

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

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Isotope (sulphur, oxygen, boron) tracing of internal or external origin of sulphates involved in the degradation of French stone monuments (BOS project)

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Key words: sulphates, salt weathering, plasters, mortars, isotopes, sulphur, oxygen, boron

1 Introduction and content

Sulphate salts crystallising in the pore space of building stones are one of the most important factors of stone monument degradation. The origin of these salts can be variable (marine, air pollution, building or restoration material) and the lack of certainty about reasons and mechanisms of solid salt precipitation represents a problem for restoration campaigns. Within the framework of the French *National Research Program on Knowledge and Conservation of Materials of Cultural Heritage*, the ongoing project BOS (2005-2006) investigates the possibility to use a combination of isotopic tracers (boron, oxygen and sulphur) to distinguish the sources of sulphate neoformation in several French monuments. The project joins restorers and researchers to assure that scientific support will help to optimise restoration strategies. The study sites are situated in a variety of lithological and climatic settings (Bourges Cathedral, Chartres Cathedral, Versailles Castle, Chenonceau Castle, and Marseille Cathedral). This fact allows comparing urban *vs.* non-polluted, marine *vs.* continental settings as well as studying a variety of building stones and restoration materials.

Previous studies using sulphur isotopes demonstrated the important role of atmospheric sulphur in black crust formation. An alternative hypothesis concerning the gypsum crystallisations responsible for the degradation of stones (scaling and spalling) consists in assuming internal sources of sulphates: Renders, bedding, pointing and repair mortars containing gypsum and other sulphate species have been frequently used during restorations and stone degradation seems often spatially linked to these materials [1]. Results obtained so far show that combining sulphur with oxygen isotope signatures provides a means for discriminating internal and external sulphate sources and the use of boron isotopes as co-tracer of salt neoformation seems promising, in particular in coastal settings where marine influence is suspected (Marseille study site).

The data from central France (Chenonceau and Bourges sites, figure 1) show clear isotopic contrasts between black crusts, which can be considered as representative of a predominantly atmospheric origin, and sulphate containing plasters and mortars. These potential end-members of sulphate contamination have distinct and well defined isotopic signatures so that the isotopic characterisation of salts in stones affected by spalling or scaling can be used to estimate the contribution of each of these endmembers.

Plasters, used rather abundantly for restauration both in Chenonceau and Bourges, fall within a range of $\delta^{18}O$ and of $\delta^{34}S$ that overlaps with the signatures of Lutetian evaporites of the Paris region [2]. Gypsum from underground quarries in Paris was a main source of plaster production in France (so-called Paris plaster) in the 19^{th} century. As the isotope ratios of seawater evolved during the earth history [3], isotope signatures of evaporitic gypsum will vary in function of the age of the evaporite formation. S and O isotopes are therefore an interesting tool to distinguish plasters of different origin [4].

Black crusts $\delta^{34}S$ and $\delta^{18}O$ values vary within a very limited range around 0 ‰ *vs.* CDT and around +11 ‰ *vs.* SMOW respectively, typical for atmospheric sulphates (air pollution).

Mortars in Bourges fall in two clearly separated groups, group 1 extremely depleted in ^{34}S and with an oxygen signature similar to those of plasters, group 2 close to the atmospheric endmember defined by black crusts. In the first case we can postulate an oxidation of pyrite contained in the marls that were used to produce the "roman cement"– type mortars in Bourges, in the second case a predominance of atmospheric sulphur. The mortars in Chenonceau contain high concentrations of gypsum and show an isotope signature identical to Paris plaster that can be considered as main compound in these mortars.

Isotopes signatures of *deteriorated building stones* from the Bourges Cathedral fall between the three endmembers "atmospheric pollution", plasters and group 1 mortars. In some cases the vicinity of plaster reparations and stone deterioration suggested direct influence of dissolved gypsum from plaster. This hypothesis could be confirmed by the isotope study. The influence of plaster is even more obvious in Chenonceau, where the isotope signatures of altered stone fall on a mixing line between atmospheric sulphates and plaster. Some stone samples show values identical to plaster leading to the conclusion that plaster dissolution is a major source of soluble salts for this monument.

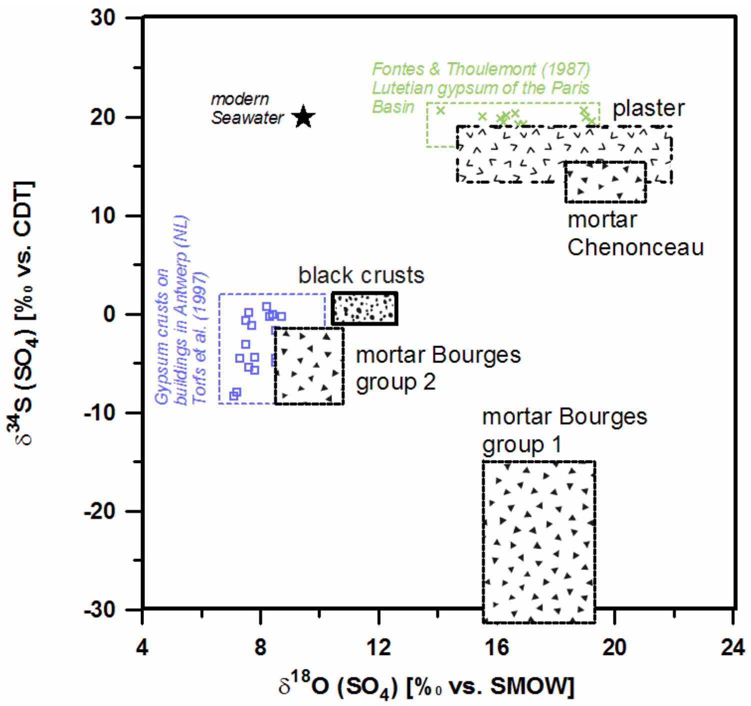

Figure 1: Range of $\delta^{18}O$ and $\delta^{34}S$ values in solid sulphates for black crusts and building materials in the Bourges Cathedral and Chenonceau Castle (France)

2 European dimension

Industrial sulphur emissions in the European Union have considerably decreased over the two decades, in particular in heavily industrialised regions like the "black triangle" of Northern Czech Republic, Southeast Germany and Southwest Poland [5]. In spite of an obvious attenuation, atmospheric pollution still has to be considered, together with marine aerosols, as a principal component of salt weathering of stone monuments and most research has focused upon these external salt sources. Internal salt sources may turn out to represent a "hidden face" of stone degradation, given the frequency of use of sulphate-containing building or restoration materials. The first results from France seem to point in this direction but even though it seems unlikely that the problem of building materials as salt sources is an isolated problem limited to french monuments, it is difficult to extrapolate them to a supranational level. Up to now, no EU wide investigation on a representative selection of sites has been undertaken.

The methodology developed and demonstrated by the BOS project which consists in combining traditional investigation methods with a set of novel isotopic tools can be adapted to a large variety of settings including monuments in continental and coastal areas. The isotopic "toolbox" could be enlarged with complementary environmental tracers (e.g. N and O isotopes of nitrate) allowing to better constrain the origin of different salts. The necessary critical mass of specialised laboratories can only be found on EU level.

3 Innovation and originality

Innovative aspects of the BOS projects lie both in its methodological and its conceptual approach.

The isotopic signatures (S, O) of sulphates derived from evaporitic rocks (sedimentary gypsum of marine origin), from anthropogenic pollution, sulphates from sulphide oxidation are clearly distinct and these isotopic contrasts have been extensively used in earth sciences and environmental sciences to differentiate the origin of sulphates. The application of these tools in the field of stone conservation is novel. Even if isotope tracers, in particular sulphur isotopes, have been successfully applied to stone degradation studies since the seventies [6, 7], studies combining several isotope tracers are rare [8] and the development of an isotopic "toolbox" containing S, O, and B isotopes has never been proposed. Combining several isotope systematics is a powerful novel approach that allows further constraining the origin of salts in building stones.

This methodology enables us to evaluate the potential role of internal sources of sulphate salts (sulphate containing mortars, plasters, oxidation of sulphides) in comparison to external sources (atmospheric pollution, marine aerosols). Few data exist on the isotopic composition of building materials [9] and their potential contribution to salt deterioration of monuments is largely unknown.

4 Impacts

The project allows enlarging the scientific basis for restoration and conservation strategies. If the potential role of certain building materials such as plasters or mortars in salt deterioration is confirmed, it might be necessary to reconsider the use of these materials or their elimination or isolation if they have been used in previous restoration campaigns.

5 Acknowledgement

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Life expectancy prediction of solid materials using chemiluminescence to characterize oxidative reactions and model-free simulation based on experimental data

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Key words: chemiluminescence, advanced kinetic analysis, model-free simulation, lifetime prediction

Abstract
Various organic materials react with environmental oxygen. They oxidise and therefore change their optical, mechanical and chemical properties. For the adequate conservation of solid materials used in art and cultural artefacts, substantial knowledge about the stability and the sensitivity to oxygen of organic materials is of particular importance.

Previous research has shown that established analytical methods such as oven-ageing tests and oxygen uptake techniques are very laborious. Furthermore, short-time experiments such as measuring the oxidative induction time OIT or – onset temperature OOT using DSC or other conventional thermo-analytical methods are unsuitable for long-term prediction of oxidative behaviour because of the use of elevated temperatures in the experimental conditions. Various studies indicate that measurement of oxidation-induced chemiluminescence can be a useful alternative to determine the stability of organic materials against oxidation.

The principle of chemiluminescence in the oxidative reactions studied is not yet entirely understood. It is believed to be a termination of two peroxy radicals in a Russel mechanism. The chemiluminescence emission results from the relaxation of excited triplet carbonyl functions ($^3R = O^*$) to its ground state.

To measure Chemiluminescence, a novel apparatus was developed at the *Berne University of the Arts* (Switzerland). Preliminary data acquired with this prototype strongly supports the use of the chemiluminescence method to characterise oxidation reactions and to determine the effects of conservation procedures on objects. Combining the insights gained under realistic conditions with an isoconversional analysis (after Friedman and Ozawa-Flynn-Wall of experimental kinetics) promises to be a powerful tool for prediction of life expectancy.

1 Introduction

Organic materials, both of synthetic and natural origin, readily undergo reactions with oxygen, even at ambient temperature. Due to oxidative degradation, organic substances change their properties. For this reason oxidative degradation is a severe conservation problem. The aim of every conservator is the prediction of long-term behaviour of any substance at given conditions. Nowadays the estimation of stability and states of degradation is an important problem for conservation scientists, trying to prevent cultural artefacts and art objects for future generations. Tools available range from sensational investigation to advanced instrumentational analysis; However, analytical results alone may well give important information on the state of preservation a substance and perhaps show some tendencies for its long-term stability. They normally do not provide any reliable prediction of long-term behaviour.

In this contribution we report on a new approach of full kinetic analysis of a solid state oxidations at moderate temperature profiles, using Chemiluminescence CL measurements performed with a newly-developed prototype instrumentation. The kinetic characteristics of the reaction were determined. The calculated kinetic parameters are subsequently employed to predict the reaction progress of the investigated samples under different temperature profiles.

2 Testing stability by high temperature methods

The characterisation of the long-term stability of organic materials requires expensive equipment and well trained laboratory staff. For stability, safety and guaranty purposes, special domains of industry are interested to describe the changes of properties of their products in dependence of the environmental conditions (temperature, time, relative humidity, UV-Vis light radiation, pollutants etc.) as well as corresponding internal factors such as mechanical stress, concentration of antioxidants etc. Scientists have developed numerous ways opportunities and mathematical models to predict the lifetime or service lifetime for specific products.

The oxidation of materials in the solid states generally occurs via the surface of the substance. That's why the oxidation reaction propagation to the bulk is diffusion controlled. Useful overviews on examination methods are given by Feller [1] Zweifel [2] and Scheirs [3]. The accelerated ageing is normally initialised by extreme environmental conditions. During the period of induction, stabilisers are consumed, the organic matrix remaining stable and keeping its properties. At the end of the induction period, when the concentration of stabilisers reaches a sub-critical level, oxidative decay starts and the substance's properties change. Frequently oxidation reactions turn out to be self-accelerating (auto-oxidation). For this reason the reaction progress may develop dramatically after the induction period.

The most common methods to test the kinetics of thermooxidative propagation of organic substances are thermal analysis methods like Differential Scanning Calorimetry DSC, Differential Thermal Analysis DTA, Thermogravimetry TG. Substances are tested using isothermal or non-isothermal temperature profiles under an oxidative atmosphere, and the time (Oxidative Induction Time OIT) or the temperature (Oxidative Onset Temperature OOT) is measured until the heat flow, ΔT (DSC, DTA) of the sample gets exothermal or the sample starts to loose its mass (TGA). In some special applications, these procedures are standardised (for example for automotive oils, cable insulations or polyolefines).

Especially for industrial and commercial applications, OIT- and OOT-procedures are widely accepted. Their advantages include an easy sample preparation, efficient measurement and established methods for data evaluation. A prominent disadvantage of these short-time experiments seems obvious: The experimental temperature must be very high (> 180 °C) for two reasons: firstly to make sure that the oxidation starts within around 2 hours and secondly to provide a distinct signal (the sensitivity of conventional instruments for thermal analysis is not adequate to the low intensity of the oxidation reaction). Diverse authors complained on the bad correlation of OIT- and OOT-data with observed long-term stabilities under normal environmental conditions [4, 5, 6]: Depending on the nature of the substance, simulations temperatures are separated from life time temperatures by one or several phase transitions. The degradation kinetics may be completely different in different phases: There is no good way to extrapolate high temperature experimental results to ambient temperature. Moreover, oxidation signals are often superposed by other thermal effects; a reliable evaluation becoming very difficult through.

Therefore alternative methods must be used for the characterisation of the long-term, low-temperature stability of organic substances.

3 Chemiluminescence method as an alternative

Luminescence is a term used for various phenomenon, originating from electronically excited states. Luminescence is a ‘cold light’, not an incandescent light. The emission of photons results from the relaxation of excited electrons (triplett-state) into their ground-state. This may be a quite quick process: the delay between the excitation and light emission is at least 10^{-10} seconds. Chemiluminescence (CL) includes all luminescence phenomena resulting from chemical reactions [7]. The fact that organic substances undergoing oxidation emit light has been recognised early on [8]. In the past few years, Chemiluminescence has gained wide acceptance as a sensitive method to study the oxidative degradation of organic solid substances.

3.1 Principles of chemiluminescence

Chemiluminescence is obey of the results of radical reactions. The first degradation step is the formation of unstable alkyl radicals, which immediately react with oxygen from the atmosphere to form peroxy radicals. These reacts further and transform into different species in an accelerating degradation cycle (auto-oxidation, left part of figure 1). Until today, the CL process is not clarified entirely within this context. It is normally attributed to a transition of excited triplett-carbonyl-functions ($^3R = O^*$) into their ground state. The spectral range of the light emitted varies according to the type of substances envolved. In most cases Chemiluminescence is located in the short wave region of the visible spectrum from 380 to 450 nm. However there are well-known exeptions: The relaxation of $^1O_2$ can be detected in the infrared region at approx. 1’200 nm).

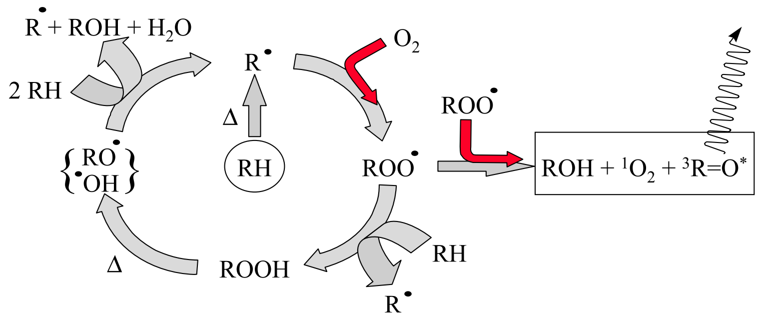

Figure 1: Simplified auto-oxidation including a Russel mechanism (from Lacey et al. [9])

The required energy (290-340 kJ mol^{-1}) may be supplied by basically three different chemical mechanisms:

- The termination two peroxy radicals in a Russel mechanism [10] is strongly exothermal (460 kJ mol^{-1}) [11]: The CL-emitter is an excited “triplet” carbonyl function (right part of figure 4.1).
- The direct homolysis of hydroperoxides followed by a cage reaction lead to an excited carbonyl-function and produces 315 kJ mol^{-1} [12].
- The metathesis of alcoxy or peroxy radicals provides 374 kJ/mol and 323 kJ/mol, respectively [13].

It have been shown, that the CL intensity reveals the existence of two kinetic stages during oxidative degradation of organic materials: The first one is correlated with the concentration of peroxide groups [14], the second stage corresponds to the oxidation propagation by hydrogen abstraction responsible for carbonyl formation [15].

3.2 CL Apparatus

The CL emission rate of organic substances close to ambient temperature is too low to be detected. For this reason, during CL- measurements samples generally have to be heated in an oven. However, only moderate heating temperatures are needed to result in detectable signals. The requirements to the oven are similar to the ones of other thermo-analytical instrumentations (such as DSC, TGA): exact control of the required temperature profile even in long-term experiments and a gas exchange facility. Additionally the sample compartment must be absolutely light-tight.

The detection of the CL-emission may be achieved using a photomultiplier tube (PMT) with photon counting mode or slow scan charged coupled device (CCD) camera. PMTs are highly sensitive devices and allow short gating times, but their dynamic ranges are low and their use must carried out with caution not to saturate the photocathode. The advantages of solid state detectors (CCDs) are their simplicity in use, their high dynamic range and the feature of imaging the sample to exhibit the inhomogeneous character of oxidation reactions. A third possibility to detect the CL-emission is to use micro channel plates (MCP) or intensified CCDs. These types of sensors offer the best sensitivity in combination with the imaging facility, but at an exorbitant price, high operation complexity and a low dynamic range.

The prototype instrumentation of the Berne University of the Arts consists of a commercial thermoelectrically cooled PMT with photon counting mode and a self built oven built chamber in combination with an optical path including a shutter system (to protect the detection unit against extensive light during sample handling and to provide background measurements). In cooperation with engineers, computer scientists and physicists, the setup of the instrumentation is actually being optimised and extended. The optimisation will include the improvement of the thermal isolation between the oven and the cooled detection unit. Moreover the development of an advanced user interface (software to control the instrumentation and to evaluate the experiments) is being realised. In the future, the instrumentation will be developed to allow for an imaging detector and for a humidity controller to moisture the samples during experiments below 95 °C. Another modification will introduce wavelength resolution to the emission experiments.

3.3 Fields of applications and experiments

Generally speaking, the oxidation of most organic substances may be characterised using the Chemiluminescence method. Our main field of application is the conservation science, but we also see applications in pharmaceutical and medical science, petrochemistry, plastics and coatings, food science, etc. At our institute, we showed the versatile nature of the CL-method in applying it to cellulose, nitrocellulose, cacao butter, natural rubber, cyclised rubber, polyethylene, polypropylene, β-carotene, etc.

The example given here is a comparison of the oxidation reactions of natural rubbers in an oxygen atmosphere: At non-isothermal experimental condition the efficiency of post-stabilising manufactured rubbers with 5% Irganox™ 565 via surface of the sample (figure 2) could be clearly shown to establish the corresponding treatment for rubber objects.

CL-data can be evaluated using the standard models already used in conventional high-temperature thermal analysis like OIT, OIT*, defining the points of interest: initial onset, extrapolated onset, midpoint, extrapolated peak, extrapolated endpoint, integration of the CL-course, first and second derivation, etc.

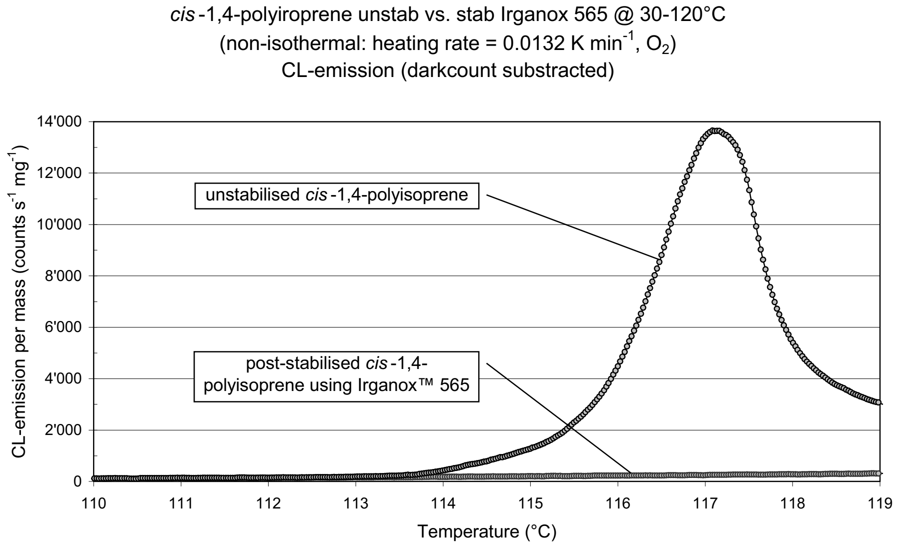

Figure 2: CL-emission normalised to the mass of unstabilised and post-stabilised natural rubber during non-isothermal experiments

Having a set of experimental data under different isothermal conditions, a standard Arrhenius-plot can be performed (figure 3).

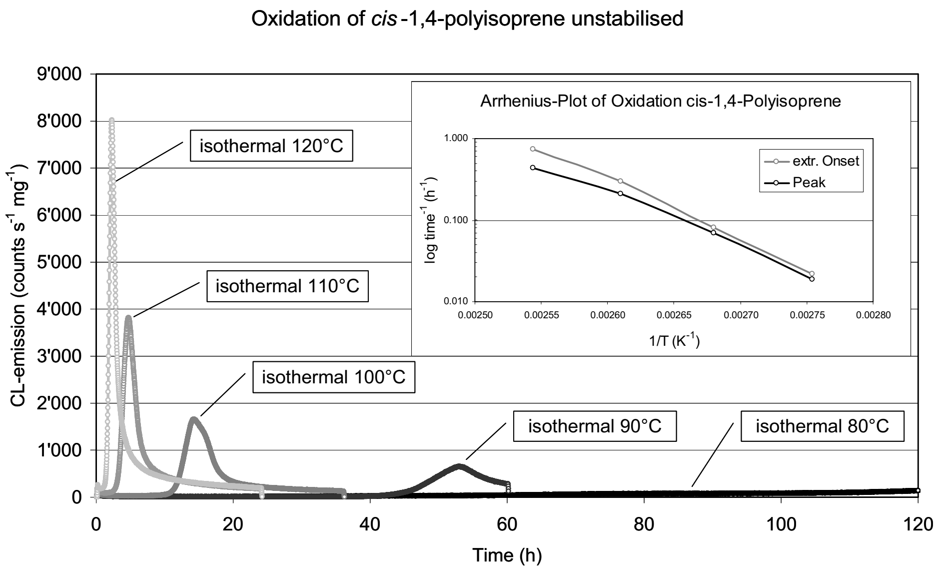

Figure 3: CL-emission normalised to the mass of unstabilised natural rubber at different isothermal experiments and the corresponding Arrhenius analysis

At higher temperatures (> 100 °C) the CL data corresponds well with the DSC data. When testing oxidative stabilities below 100 °C, the limitations of DSC become obvious: Because of its low sensitivity, DSC is unable to provide useful information (figure 4).

The DSC experiments were performed on a Mettler Toledo DSC822e using the STARe-software version 8.10.

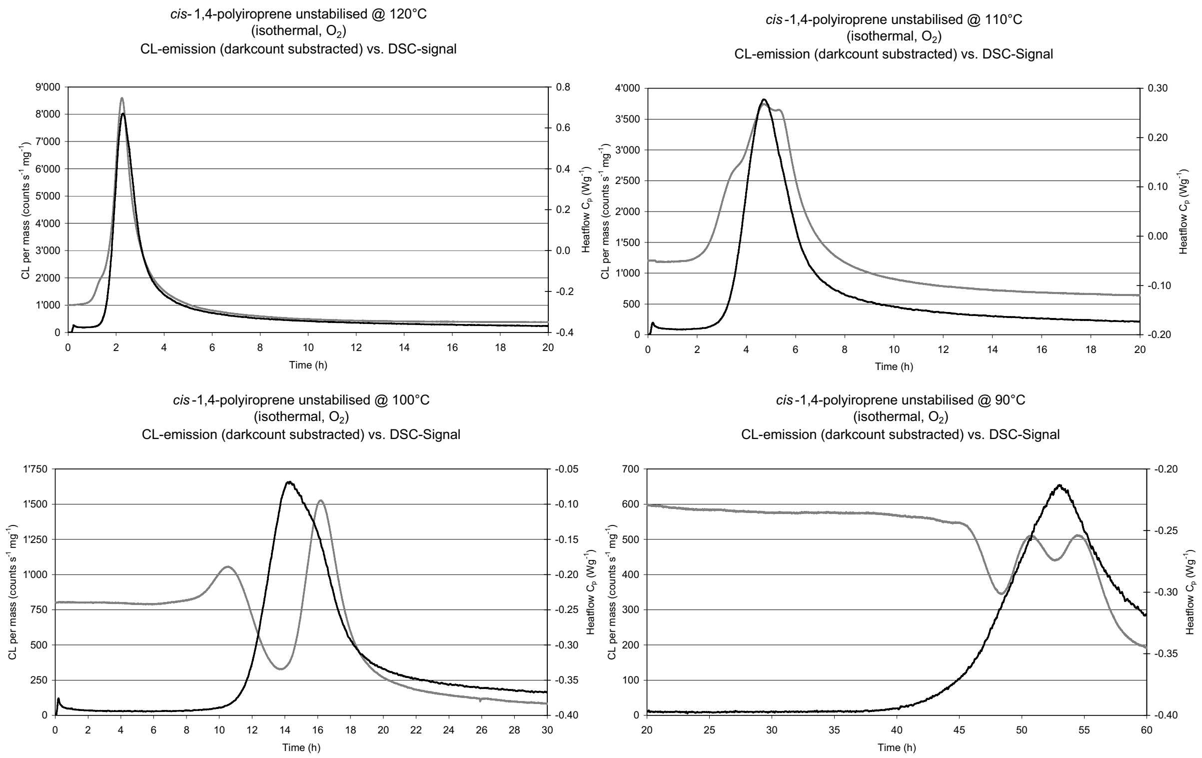

Figure 4: Comparison between CL-emission (black lines) and DSC-heatflow (grey lines) at different isothermal conditions (120, 110, 100, 90°C) to reveal the limitations of conventional thermal analysis for stability characterisation at low experimental temperatures.

3.4 Advantages of CL

Compared to DSC and other conventional thermal analysis, CL offers many advantages: With its much higher sensitivity, experiments can performed at much lower temperature profiles, i.e. closer to the real degradation conditions. This fact is of importance for the characterisation of substances with low temperature melting points, glass transitions, etc. The outstanding baseline stability of CL is of great benefit when performing long-term experiments [16]; the CL-signal is moreover related exclusively to oxidation processes and therefore not superposed by other type of reactions.

The instrumentation setup may be designed individually for special fields of applications and goals of research: For lower temperature as 95 °C, the conditioning of reaction gas with humidity as relevant oxidative factor bears great promise. The heterogeneous nature of solid state oxidation can be effectively investigated using imaging detection devices; with the use of spectrometric devices one can gain for advanced basic research detailed information about the mechanistic of oxidation.

Measurement of sample particles less than 0.5 mg can be easily performed. A basic instrumentation would not be more expensive than a commercial DSC apparatus.

4 Advanced kinetic analysis and lifetime prediction

Generally kinetic analysis of decomposition processes can be applied to any type of thermoanalytical data (DSC, DTA, TGA etc.) for the study of raw materials and products within the scope of research, development and quality assurance. The technique provides a means to infer additional characteristics and behaviour of examined substances based on thermoanalytical measurements. The experimental procedure starts with the determination of quantifiable parameters, directly related to the degradation kinetics for a given substance. These parameters are then used to predict reaction progress under various temperature ranges and conditions. Generally, direct investigation of the reaction is very difficult at low temperatures (requiring very long measurement times), as well as under complex temperature profiles. Applying Thermokinetics software (www.akts.com), the rate and the progress of the reactions can be predicted on the basis of various well-defined temperature profiles [17].

A full kinetic analysis of a solid state reaction has at least three major stages:

- experimental collection of data;
- computation of kinetic parameters using the experimental data; and
- predictions of the reaction progress for required temperature profiles applying determined kinetic parameters.

In this contribution we report on a new application of this approach to investigate the thermo-oxidative stability of solid states at moderate temperature.

5.1 Determination of the kinetic characteristics: theory

The noticeable weakness of the 'single curve' methods (determination of the kinetic parameters from single run recorded with one heating rate or isothermal condition only) has led to the introduction of 'multi curve' methods over the past few years, as discussed in the International ICTAC kinetics project [18, 19, 20, 21].

The isoconversional methods extensively studied by Friedman [22] and Ozawa-Flynn-Wall [23, 24] were applied in the following prediction. A detailed analysis of the various isoconversional methods (i.e. the isoconversional differential and integral methods) for the determination of the activation energy has been reported in the literature by Budrugeac [25]. The convergence of the activation energy values obtained by means of a differential method (Friedman) with those resulted from using integral methods with integration over small ranges of reaction progress α comes from the fundamentals of the differential and integral calculus. Friedman analysis, based on the Arrhenius equation, applies the logarithm of the conversion rate $d\alpha/dt$ as a function of the reciprocal temperature at different degrees of the conversion. As $f(\alpha)$ is constant at each conversion degree α_i, the method is so-called 'isoconversional' and the dependence of the logarithm of the reaction rate over $1/T$ is linear with the slope of $m = E/R$ as presented in figure 6 (left part). Degradation reactions are often too complex to be described in terms of a single pair of Arrhenius parameters and the commonly applied set of reaction models. As a general rule, these reactions demonstrate profoundly multi-step characteristics. They can involve several processes with different activation energies and mechanisms. In such situation the reaction rate can be described only by complex equations, where the activation energy term is no more constant but is dependent on the reaction progress α ($E \neq const$ *but* $E = E(\alpha)$).

The accurate determination of the kinetic parameters under experimental conditions applied, which enables the correct fit of the experimental data, is a prerequisite for prediction of the reaction progress under any new temperature profile. However, it is important to note that the baseline construction can significantly influence the determination of the kinetic parameters of the reaction. Therefore, when solving the complicated interrelation between the baseline, the kinetic parameters of the reaction and reaction progress, other considerations can be made besides the isoconversional approach to improve the determination of the kinetic parameters. Moreover, the correct baseline determination should be intimately combined with the computation of the kinetic parameters for the investigated reaction.

5.2 Results

The data collected during the experiments carried out with different isothermal conditions (figure 5, left part) were used for the determination of the kinetic parameters used later for the prediction of the reaction progress.

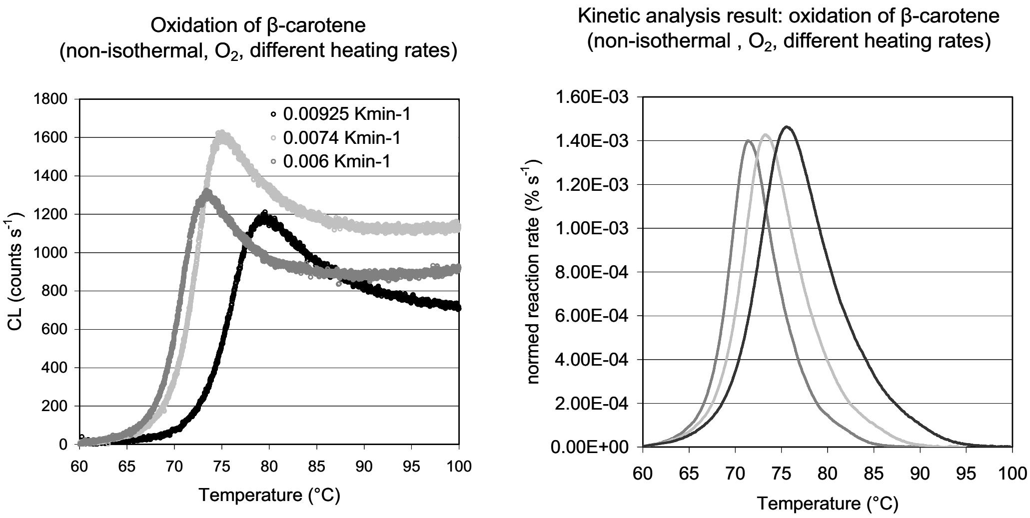

Figure 5: Experiments of β-carotene oxidation characterised with Chemiluminescence (left part) and kinetic analysis result after baseline optimisation (right part performed with AKTS thermokinetics software, www.akts.com)

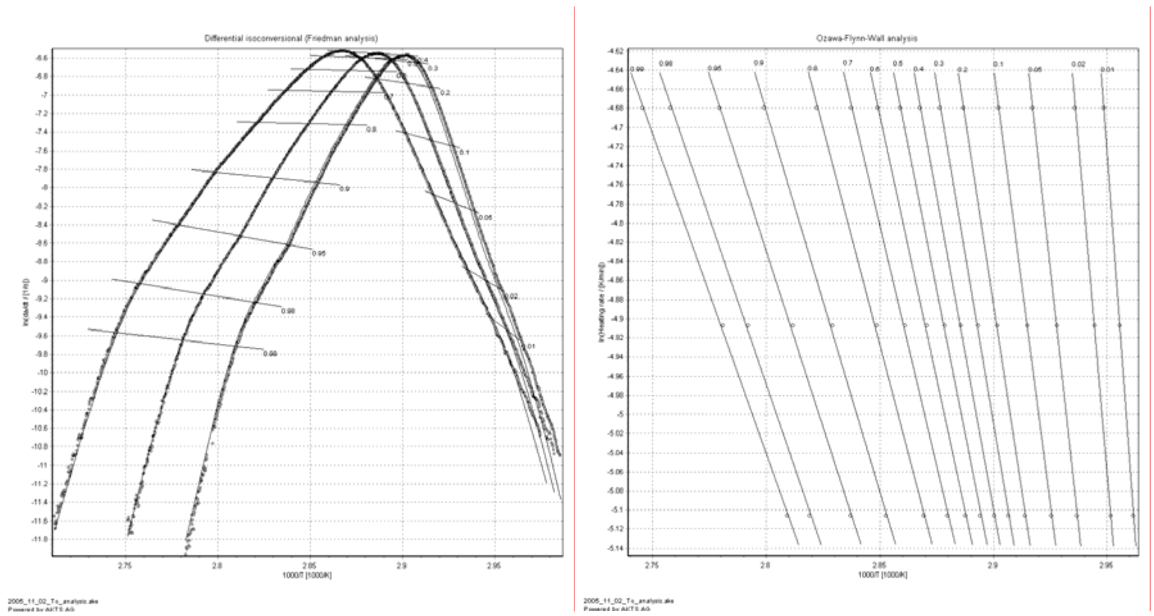

Figure 6: Differential isoconversional analysis after Friedman (left part) and Ozawa-Flynn-Wall analysis (performed with AKTS Thermokinetics software, www.akts.com)

Once the kinetic parameters are determined (figures 6, 7), the method can be applied to predict the evolution of the substances oxidation under different temperature profiles (figures 8, 9). This influence of ageing can again observed by predicting the reaction progress under e.g. isothermal conditions. For the β-carotene sample, the maximal rate of thermal degradation occurs after the induction phase. The reaction progress extends therefore over years. After exceeding the oxidative induction period, the lifetime of the substance have elapsed.

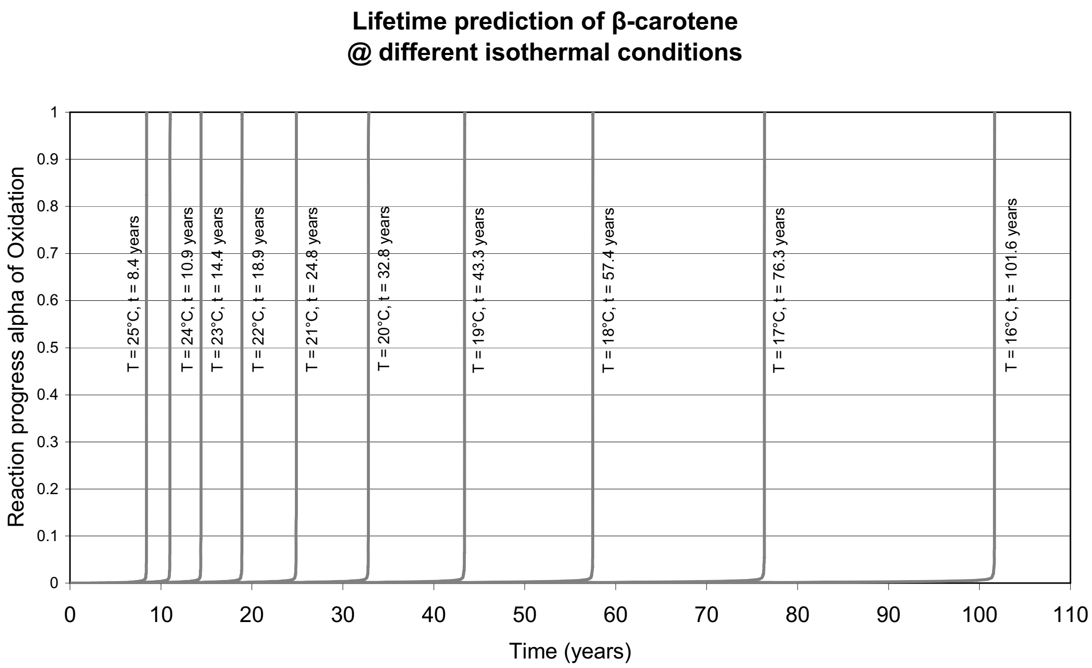

Figure 7: Activation energy of β-carotenes oxidation kinetic according to Friedmans differential isoconversional analysis (performed with AKTS Thermokinetics software, www.akts.com)

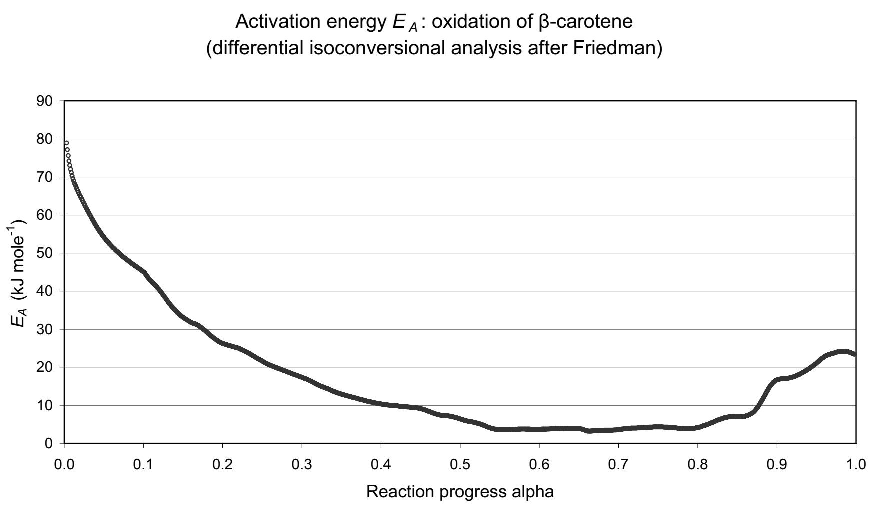

Figure 8: Predicted oxidative reaction progress (lifetime prediction) of β-carotene at given isothermal temperature conditions: 16-25 °C (performed with AKTS Thermokinetics software, www.akts.com)

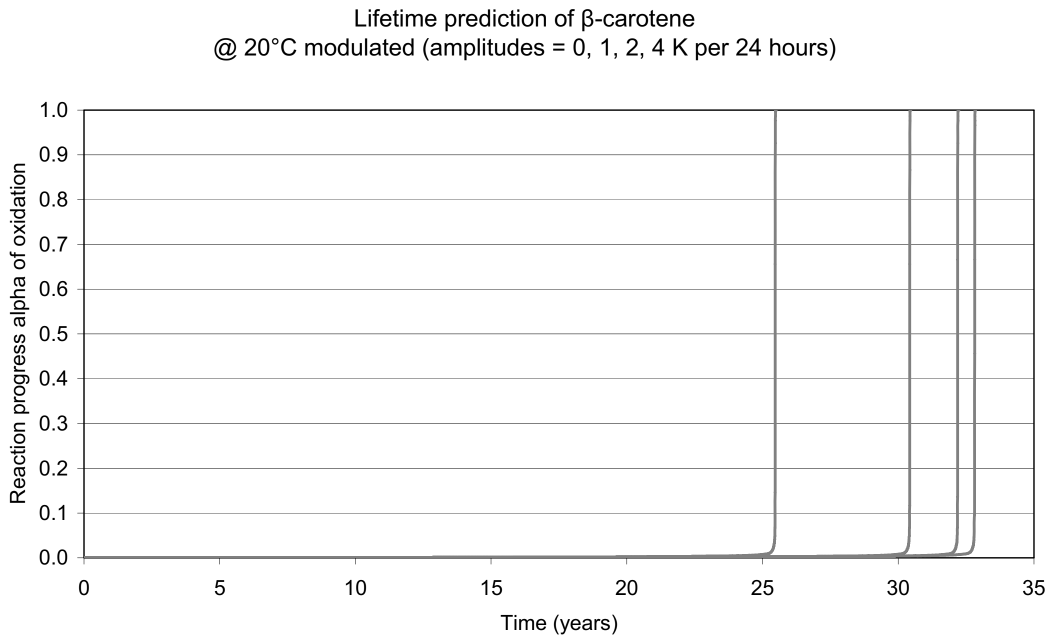

Figure 9: Predicted oxidative reaction progress (lifetime prediction) of β-carotene at given modulated isothermal temperature conditions: 20°C, amplidudes 0, 1, 2 and 4 K per 24 hours (performed with AKTS Thermokinetics software, www.akts.com)

5 Conclusions

This contribution reports a new experimental setup to predict oxidation kinetics and stability of organic substances at low temperatures. The procedure consists of experimental data acquisition using the Chemiluminescence method because of its outstanding sensitivity and advanced numerical techniques with isoconversional analysis of the reaction kinetics. It has been shown that the setup can be used in the context of conservation-restoration to obtain precise information about stability of different organic substances with regard to their oxidative decay and/or to assess the effects of conservation-restoration treatments (e.g. the deacidification of paper, the invasive post-stabilisation of natural rubber objects, etc.).

The reported applications of CL are just some first examples to demonstrate the high potential of the Chemiluminescence method on the one hand and the approach of lifetime prediction on the other hand.

6 European project details

The reported approach is subject of a research programme 'Kinetics' at Berne University of the Art – BUA (Commission for applied research and development: 5000PT.HKB). FK planed, designed and executed the CL instrumentation and acquired the experimental data. BR developed the software thermokinetics and computed the analysis. SW is the Co-ordinator of the kinetics research programme at BUA.

There is actually no direct connection to any European projects.

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Enhanced optical methods for analysis of historical objects

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Key words: diagnostics, optical methods, cultural heritage, radiography, micro-CT, photometry stereo

Introduction

The paper presents a review of special optical research infrastructure developed for analyses of historical objects and materials.

First, new methods for analysis of surface qualities and micro-geometry are shown. They posses a capacity to replace empirical quantification rules build upon comparison between learned judgment of experts by quantitative data acquired from studied surface, which is applicable mainly in research into the soiling problems, surface degradation development monitoring, finger prints of small objects as, e.g. coins, cuneiform tablets documentation and virtual presentation for reading, checking and control of façade cleaning processes, etc. The developed technique and evaluation tools are capable to describe and measure three dimensional deformation of surfaces and their application goes far beyond the cultural heritage problems. The method is applied and demonstrated on stone and mortar surfaces of selected cultural heritage monuments in the Czech Republic.

The next part deals with enhanced X-ray diagnostics methods. It starts with application of portable x-ray source and super flat flexible recording plates for multiple use, which is suitable mainly for investigation and surveys of historical timber structures and this is demonstrated on some Czech and US examples.

The last part presents development in the field of digital micrometric high resolution X-ray transmission radiography and tomography which provides high quality micro radiographs of small objects including very low contrast and low absorption ones.

1 Optical methods

A notion 'optical methods' is used in a broader sense in this paper. These are not only methods studying the object's properties in visible light, but many other methods as well. The result of such methods is information interpreted visually like image based on perception of color and patterns, it can be an enhanced image, and computer / equipment assisted vision or quantification of visual field. Other representations include augmented reality, multi-spectral vision, VR.

Optical methods can be used for analysis, documentation and monitoring. Some methods implement principles of human vision when identifying object in the image. Investigation of medieval mortars reinforced by goat hairs can serve as an example. In order to find out mechanically equivalent replacement, properties like Young modulus and strength of hairs had to be determined. Obviously, it is not possible to place such a delicate specimen into tensile testing machine. An alternative approach had to be adopted using optical identification method to track marks on the goat hair as a measure of elongation response to added weight load [1].

1.1 Coded photometry stereo (CPS)

The methods utilizing relation between observed relative brightness of the surface and angle between direction of incident light and surface normal at given point are known as Shape from Shading and Photometry Stereo methods [2-4]. The roots of these methods can be traced to the astronomy as a useful tool for study of planets' topography. The slopes in two orthogonal directions and surface color at given point form a set of three unknowns. In order to obtain a unique solution for these unknowns a system of three equations has to be formed using three different lights for surface illumination. For various reasons it is always advantageous to prefer a solution capturing the three independent scenes at once. One possible way how to do it, is to store three scenes illuminated by three monochromatic lights R G B simultaneously, using a digital camera equipped with a Bayer filter separating image into the same R G B color channels. This is the way we ENcode the three scenes into one image. Later, during computer processing the image is again DEcoded and treated as three images. The device is shown on Figure 1.

Figure 1: A laboratory version of CPS device shown with a calibration specimen

1.2 Use of CPS

The CPS method was originally developed during work on project HISTOCLEAN for the purpose of laser cleaned surface evaluation [6]. The issue of surface cleaning of cultural heritage objects is very important for their proper function. It is interesting that the above described principle is behind both surface quality evaluation and the process running in viewer's head while looking at a statue. It is due to the fact that our eye enjoys shape complexity of statues using the same principle. It is quite interesting that the method utilizes similar principles of decoding visual field as a human eye uses for "reading" shapes in everyday world. That is why the volume information disappears when the statue surface is darkened by crust in such a level the eye is no more able to distinguish levels of shadow.

At the present time the CPS method is used in conjunction with other optical methods as a tool for determination of complex 3D displacement field in the vicinity of a crack tip [6]. There are many other applications for this method waiting to be discovered. For example, in a collaboration with Dept. of languages of ancient Middle East of Charles University, we are about to start a joint project on scanning their collection of Cuneiform Tablets to make their virtual copies available to researchers in the form suitable for reading and studying the texts. The problem with scanning the tablets is that scanning cancels shadows of wedge-shaped letters that are, actually, a guide for reading the script (see Figure 2).

The CPS method seems a perfectly suited to perform the task, as it is possible to separate natural color variation in material from shadows casted by grooves forming the tablet topography. In a final step it is possible to introduce an artificial lighting in the scene to replicate the process the reader actually uses while reading the tablets. The other use of the method can be Braille alphabet, other flat objects with fine relief like coins, seals.

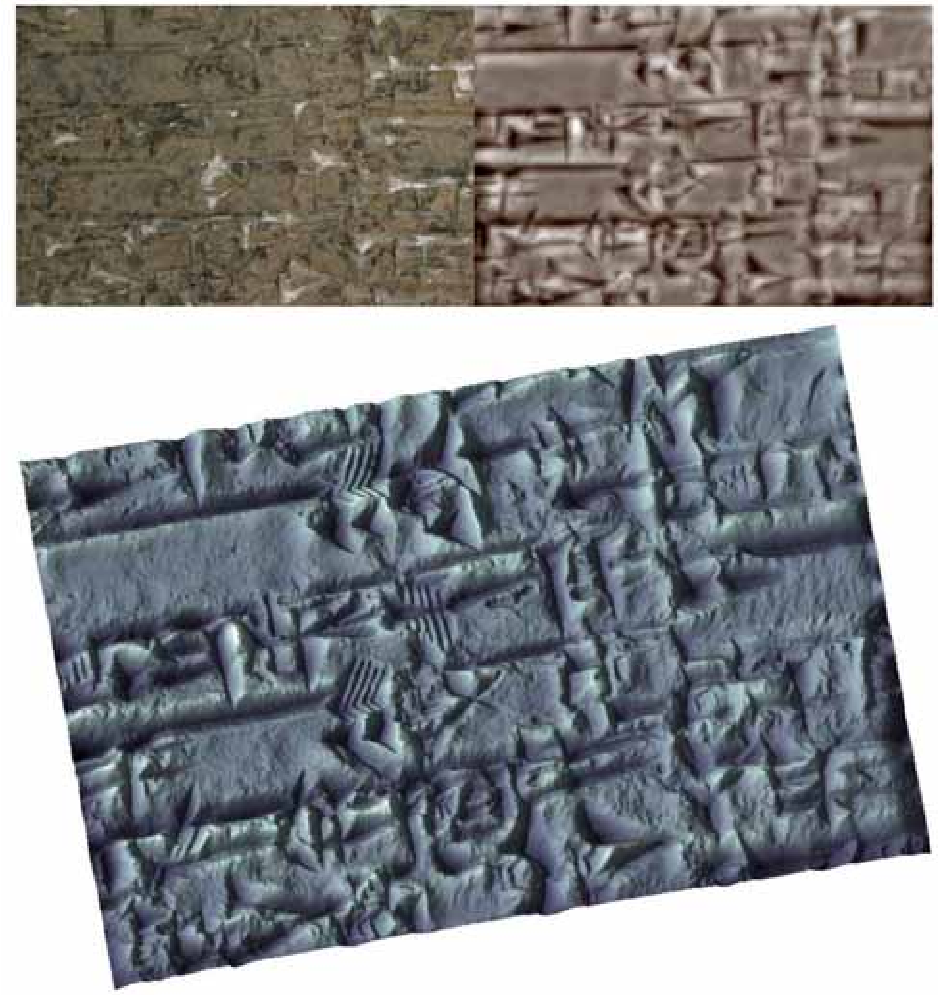

Figure 2: An application of CPS on reconstruction of 3D topography of cuneiform tablets topography. Top-left depict original photography of the tablet, top-right image represents color-coded depth distribution on the tablet surface and bottom axonometric view

1.3 Optical scanner

Another example, of turning image into information, is a use of a simple portable scanner for evaluation of soiling of the historical buildings' surfaces. Once a reproducible light intensity is provided by the system illumination, it is possible to measure surface reflectance and color variation reliably. The time series of the measurement records for monitoring purposes and even for prediction of the time for a renovation can be used. The aim of the study was to correlate public opinion with some quantitative measurable values. It turned out that dispersion of point cloud of brightness-saturation axis representation of a scanned surface is a useful measure of surface degradation as seen on Figure 3. The statement is especially valid for painted façades (manifesting consistent optical homogeneity) on baroque churches and palaces abundant in Prague. For natural stones – limestone and mainly sandstone – a reference place has to be selected for monitoring.

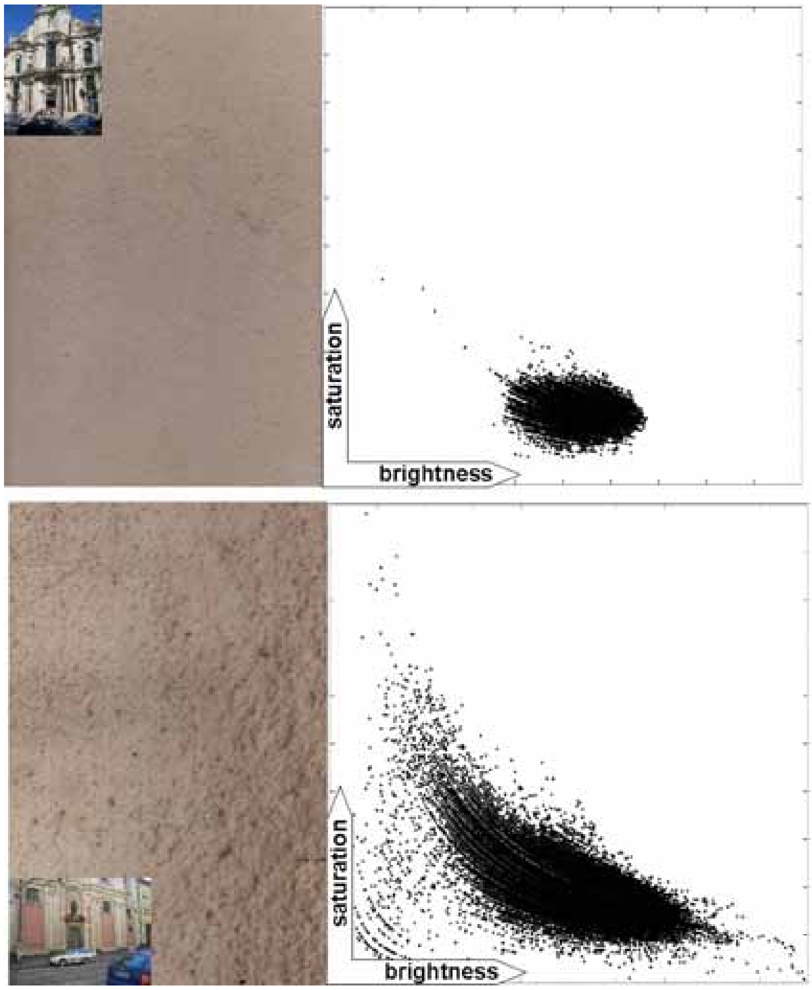

Figure 3: Comparison of scans of two facades with analysis of brightness - saturation distribution. The 'dispersion" of the cloud of points below indicate polluted surface

2 X-ray methods

2.1 X-ray radiography

To demonstrate a palette of applicable methods used for investigation of CH objects, one has to mention here also X-ray radiography which is not optical method considering a wavelength of used rays. But at the end of process chain is invisible made visible by formation of an image on a flat recording plate or converting detector signal into viewable image. The penetrating character of rays enable observer to see what is inside based on contrast implied by different radiation absorption of atoms of materials. The principal conditions required to achieve high resolution X-ray imaging (i.e., in the micrometric scale) are a high performance X-ray detector and a "point" source (or collimated) X-ray beam. The experimental system for micrometric resolution digital X-ray transmission radiography has been successfully realized and tested on a number of different objects. Excellent quality micro roentgenograms are obtained even on extremely low contrast and low absorption objects using Direct Thickness Calibration Method. This method effectively corrects for both individual pixel efficiency and beam hardening effect simultaneously.

Such a set-up can reveal, for example, how frescos in Veltrusy castle are attached to the ceiling, or X-ray radiography proves an indispensable tool for examination of a state of a timber framework supporting church roof. Radiogram and image in pseudo-colors depict the same area. The spot in the color image indicated decrease in material density and therefore decrease in load supporting capacity of the element [7].

2.2 Micro-CT

A micro tomograph for analysis of the inner structure of small specimens was developed in collaboration with the Institute of Experimental and Applied Physics. In contrary to commercial CTs where X-ray source and detector rotate around studied object, in adopted design the specimen is rotating while source and detector are motionless. Fine tuning of X-ray source with a specialized calibration process of Medipix X-ray detector can increase sensitivity and resolution of the device at level comparable to the devices equipped with a synchrotron source. One possible application of such device is composition study of mortars enabling direct calculation of constituents (phase) volumes expressed in number of voxels. This approach is much more straightforward in comparison to methods of composition estimation based on area measurement in cross-section and followed by volume calculation. Other topic suitable for this kind of experimental investigation is cracks and void concentration evaluation in a small specimen extracted from the bulk. On the image small block of concrete of the size 2 × 7 × 13 mm is shown. The pores and inclusions detected resemble small bubbles – it is possible to see their shape and distribution thorough the volume as Figure 4 shows.

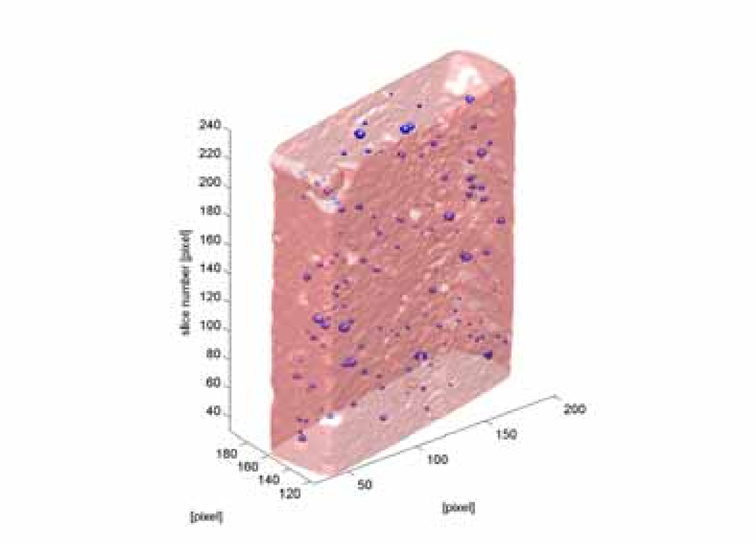

Figure 4: Micro CT of small concrete block showing inner pores and grains

3 Conclusions

A simple adaptation of existing optical methods can yield new and interesting results which cannot be obtained other way. But not only the methods are a key to the success, it is the whole infrastructure, which has to be understood in broader sense. Infrastructure is also a team of skilled experienced people coming from various scientific fields working together on innovative implementation of ideas and procedures in new applications in addition to sum of equipments, devices and existing methods. They can adopt methods used in other field to respect specificity of historical objects and enhance them.

As demonstrated on above described examples, it seems that these methods – sophisticated and yet simple can be indispensable for research in the field. They offer results impossible to obtain by other means. Unfortunately investment into such methods hit a 'blind spot' of research funding system – are too expensive and therefore behind reach of a single institute to finance them using only its own resources and, at the same time, to small to be given attention of decisive funding agencies.

4 Acknowledgement

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Large scale investigation of bronze archaeological artefacts from Mediterranean basin

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Key words: corrosion, patina, bronze artefacts, SEM+EDS, XRD, optical microscopy

1 Introduction

The development of innovative and tailored strategies and products for the long-term stable conservation of archaeological Cu-based artefacts needs to identify the origin of degradation phenomena and its relationship with the archaeological environment.

In the framework of the EFESTUS project, archaeological areas of the Mediterranean basin and well-defined and coherent groups of copper-based artefacts found there, have been selected in order to study degradation cases, representative of the different Mediterranean deterioration phenomena. The guidelines for selecting artefacts have also considered their use, manufacturing technique, expected chemical composition and metallurgical structure as well as the soil nature. This approach is justified considering that the data base currently available from literature, is often only a juxtaposition of results obtained by adopting different analytical and methodological approaches and by studying large numbers of individual artefacts of all kinds, not related to archaeological contexts or to the intrinsic metallurgical or chemical features of the artefacts [1-4]. In some cases, phenomenological models have been also proposed and classes of corrosion structures were defined in order to explain the formation corrosion layers, even though some deviations and discrepancies have been pointed out by the same authors [5].

With these consideration in mind, archaeological contexts and copper-based artefacts found there have been selected as representative of the different Mediterranean situations, and have been studied by systematically using the same methodological approach and analytical techniques, as scanning electron microscopy combined to energy dispersive spectrometry (SEM-EDS), optical microscopy (OM), X-ray diffraction (XRD), inductively coupled mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS).

The description of the archaeological contexts and the chemical, micro-chemical and micro-structural results obtained from the more significant and representative 70 artefacts and 12 archaeological soils is reported in the EFESTUS project Anglo-ArabicWeb Site (www.efestus.just. edu.jo).

2 Experimental

The chemical composition, corrosion product nature and microstructures were studied by X-ray diffraction (XRD), inductively coupled mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS).

Both SEM and EDS characterisation were carried out by using a Cambridge 360 scanning electron microscope equipped with a LaB6 filament and a four sectors back scattered electron detector. The samples have been coated with a thin layer of carbon in order to observe the samples without charging effects. The carbon coating was deposited by using an Emitech sputter coater K550 unit, a K250 carbon coating attachment and a carbon cord at a pressure of 1×10^{-2} mbar in order to produce a carbon film with a constant thickness of about 3.0 nm.

The surface morphology of the samples has been observed by using an optical microscope Leica MZ FLIII or a Nikon apparatus equipped with a digital camera. OMinvestigation of cross-sectioned samples has been carried out by using a Leica MEF 4 microscope equipped with a digital camera. In order to prepare the cross sectioned materials, representative fragments of bronze artefacts were embedded in epoxy resin with a setting time of 24 hours and sectioned by using a diamond saw in order to preserve the corrosion products. The sections were polished with silicon carbide papers upto 1200 grit and the final polishing was performed with diamond pastes up to 1/4 μm in order to have mirror like surfaces on the sections. X-ray diffraction patterns were recorded directly on the ancient bronzes, by multiple scanning using an automated Seifert XRD-3000 diffractometer. The identification of the species was carried out by using a Seifert 3000 Software Index I.

3 Results and discussion

In Fig. 1, some of the selected copper-based archaeological artefacts are shown. The selected artefacts have been recently found during the excavation of 12 archaeological areas representative of possible different Mediterranean contexts, including desert areas in Jordan, Tunisia and Egypt, continental sites, corrosive marine environments located on coastal areas (S. Antioco and Tharros, Sardinia, Italy) and the riverbanks of a big ancient city as Rome.

Figure 1: Archaeological copper-based artefacts found during the excavation in the Ayanis fortress (Turkey), the lion head (left), and in Tharros, Sardinia (Italy), the Roman coin (right)

Carthage (Tunisia) the most important Punic city was also considered together with the Anatolian city of Ayanis (VII cent. BC) whose fortress is at 1866 m above sea level, and where snow usually stays for five or six months. The soils of the archaeological contexts have been sampled and analysed. It is worth noting that the selected Cu-based archaeological artefacts have been produced by using the main manufacturing techniques employed in ancient times to produce bronze artefacts and include casting in moulds, lost wax casting, minting, and cold and hot mechanical shaping. The ancient original use of selected archaeological artefacts was different being artistic, ritual, common use objects, coins, weapons, cosmetic tools, mirrors and jewels.

Their chemical composition is wide and includes all kinds of ancient Cu-based alloys such as copper, low tin and high tin also leaded materials and Cu-Fe alloys. The chemical composition of the bulk metal of the 70 most representative selected artefacts shows a very large variation of the content of the alloying and minor elements copper is the main component of all the archaeological alloys that in some artefacts can be assigned to the leaded bronzes class because the Pb content ranges from 6-8 wt.% to about 27 wt.%.

Tin is present in largely different amounts in all the samples and ranges from 0.5-31 wt.%. The wide variation of the tin and lead content indicates the tailored use of different materials to produce artefacts to be differently utilised. Tin is the main alloying element for producing bronze and its increasing amount consequently increases the mechanical properties of the bronze even though, the Sn content generally does not exceed the 8-10 wt.%. Indeed, bronzes containing much more 10 wt.% cannot be satisfactorily worked without some danger of breaking, due to the formation of the hard and brittle (α+η) eutectoid phase in the bronze.

Lead is a common addition to bronze carried out in antiquity for producing objects characterised by low mechanical properties to be utilised at room temperature. Indeed, an addition of lead up to 2% improves the fluidity of the melted bronze alloy [10, 11] even though, a loss of mechanical properties could be induced, and if the lead amount is increased up to 3-4 wt.%, hardness and toughness are consequently reduced. With higher amounts of Pb, a remarkably deterioration of mechanical properties is produced and the only derived advantage is the low cost of lead with respect to the more expensive and rare tin. The loss of mechanical and thermal features is well explained by the copper-lead diagram. Indeed, because lead has substantially no solid solubility in copper and copper-based alloys, if the percentage of lead in bronze is higher than a few percent (pct), lead occurs as a dispersion of fine particles throughout the bronze [7-9]. The number of the lead particles and its distribution as globules in the copper matrix vary as a function of the lead content and casting parameters thus giving rise to the formation of a material constituted by a copper matrix where lead islands are scattered. The resulting effect of the presence of lead on the microstructure of the bronze artefacts, can be seen in Fig. 3, where a back scattered electrons image of a cross-sectioned low-leaded bronze Punic coin is shown. From a compositional point of view, the lead data reported in the histogram of Fig. 2, are comparable with the chemical composition of the Etruscan, Greek and Italic bronze objects, and with the small amount of literature data concerning the lead content of the Phoenician-Carthaginian artefacts from Spain [7-11], whereas the Sardinian items have generally a lower lead content [10, 11].

Another common trace or minor element in Cu-based artefacts is iron, which is mainly present with copper as copper- iron sulphides or as an iron oxide. This element could come from the impure copper ore or from the fluxing compounds used during the smelting process and as pointed out by Craddock [10, 11] the iron content could be used as technological indicator of the smelting process.

An amount of about 0.05 wt.% is typical of the early processes carried out under poor reducing conditions, while content higher than 0.3 wt.% indicates a more efficient process and therefore, the iron content could evidence the advanced technological competency and skill of the smelting operator.

Also for iron, the EFESTUS results are comparable with those obtained from bronze Etruscan, Greek and Roman objects [10, 11], except only for few Punic coins found in Sardinia which have a relevant content of iron associated in some cases with a low amount of cobalt. As for silver the results indicate how its variation is within narrow limits from 0.007 wt.% and 0.18% and that artefacts with a lead content higher than 2 wt.% have generally a low silver amount ranging from 0.007 wt.% to 0.05 wt.%.

On the contrary, the artefacts with a silver content ranging between 0.05 and 0.18 wt.% are characterised by a lead content lower than 2.0 wt.%. This result suggests that silver comes more likely from the copper ores than from the added lead [12].

The zinc content ranges from 0.01% to 0.96 thus indicating the use of copper ores with variable content of zinc sulphide.

The arsenic and antimony amount of the EFESTUS artefacts varies from 0.01 wt.% to 0.62 wt.% and 0.01 wt.% to 0.21 wt.%, respectively, thus confirming relevant differences in the alloying and refining practices. The arsenic and antimony amounts indicate that the copper has been obtained from the use of a sulphide ore, which was not completely roasted [10] and in some cases raw refining techniques.

The above reported results indicate the presence of variable amounts of impurities most of which could be reduced to acceptable levels [11] quite easily by melting the copper or the bronze in an open crucible and allowing the unwanted elements to oxidise, to float to the melted surface and be skimmed off. Therefore, the results indicate that refining processes have not always been carried out before casting, and that raw bronzes were used for producing many of the selected artefacts. Refined materials were used only for producing weapons such as shields, dagger and helmets that have been manufactured by utilising alloys with well-controlled chemical composition.

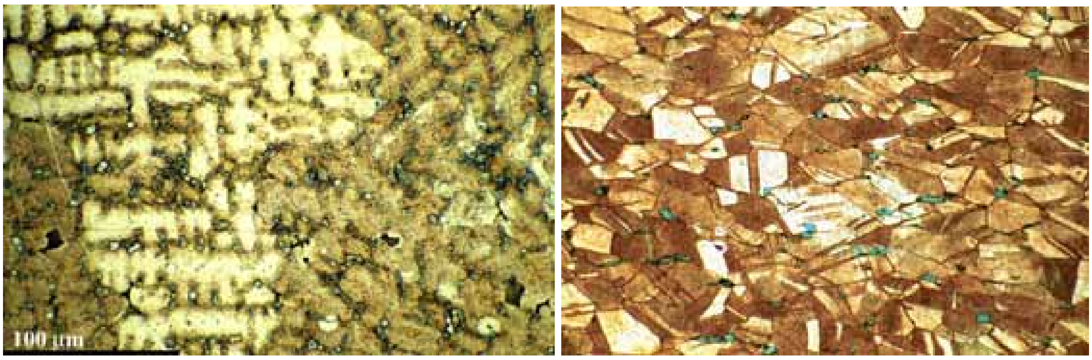


Figure 2: Cross-sections of archaeological artefacts found at Tharros (Sardinia, Italy). The images show typical examples of the different metallurgical features observed in the EFESTUS Cu-base selected archaeological artefacts. In the dendritic matrix lead islands and Cu-Fe sulphides are present (left). The right image shows a well-crystallised matrix characterised by the presence of twinned grains with different size and slip lines.

The metallurgical features of the selected artefacts have been investigated and some results are shown in Figs. 2 and 3.

The images displayed in Fig. 2 have been obtained from a Punic coin and a nail. In the matrix, of the dendritic structure, small scattered lead islands and Cu-Fe sulphides are present. The right image shows another example of the typical structure of well shaped artefacts obtained via repeated cycles of mechanical working and hot treatments, a well-crystallised matrix is present, and is characterised by the presence of twinned grains with different size and slip lines.

In Fig. 3, an uncommon example of ancient metallurgical structure is shown: the micro-chemical structure of a crosssectioned *Aes rude* found at Terrasebis (Sardinia, Italy). The back scattered electron (BSE) image and the ED spectra, not reported for brevity, show the presence of circular to elliptical α-iron spheroids scattered in the copper matrix, the white interdendritic phases consist of lead.

These unworked lumps of Cu-based materials i.e. *Aes rude*, have been found in many Italian archaeological sites and dated between the sixth and third centuries BC. Archaeological considerations indicate *Aes rude* have been appreciated as currency, as a medium of exchange and as a form of saving, and the micro-chemical investigation of these artefacts discloses their apparent unusable nature for any other functional applications or possible use. Indeed, Aes Rude appear as copper materials but micro-chemical results indicate that they consist of a highly ferruginous leaded copper and therefore, they are useless for producing other metal objects via casting or hot and cold working. Notwithstanding this intrinsic negative feature, the production of these intractable Cu-based alloys was deliberately carried out in ancient Italy for maximising the process yield in terms of produced metal from an impure and unselected metal ore by tailoring the smelting process parameters.

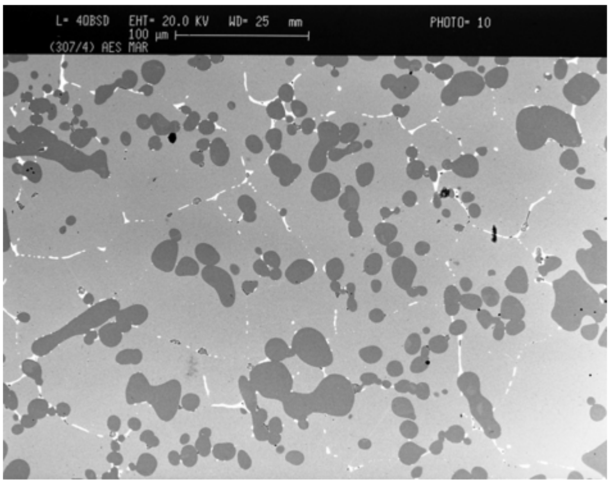


Figure 3: Micro-chemical structure of a cross-sectioned Aes rude found at Terrasebis (Sardinia, Italy). It can be observed the presence of circular to elliptical α-iron spheroids scattered in the copper matrix, while the white interdendritic phases are constituted by lead.

With this consideration in mind, the micro-chemical investigation of these ancient iron-copper alloys i.e. *Aes rude*, give evidence of the passage from the acceptance of an artefact value based on its true nature or potential use to the acceptance of the value based only on its appearance or form independently from its present or future use.

The large-scale characterisation has also documented the complex micro-chemical structure and nature of the corrosion products grown during the long-term archaeological burial, and has indicated that the artefacts suffer from an intense and selective dissolution of copper that in many cases induce the formation of a stratified structure, whose internal zone is mainly composed of cuprous oxide and copper chlorides. The results obtained in the framework of the EFESTUS project have also shown that the worked and shaped artefacts via thermo-mechanical treatments are heavier affected by the copper degradation induced by chlorine. The nature of corrosion products have been studied by means of XRD and the results have provided good insight into the corrosion layers.

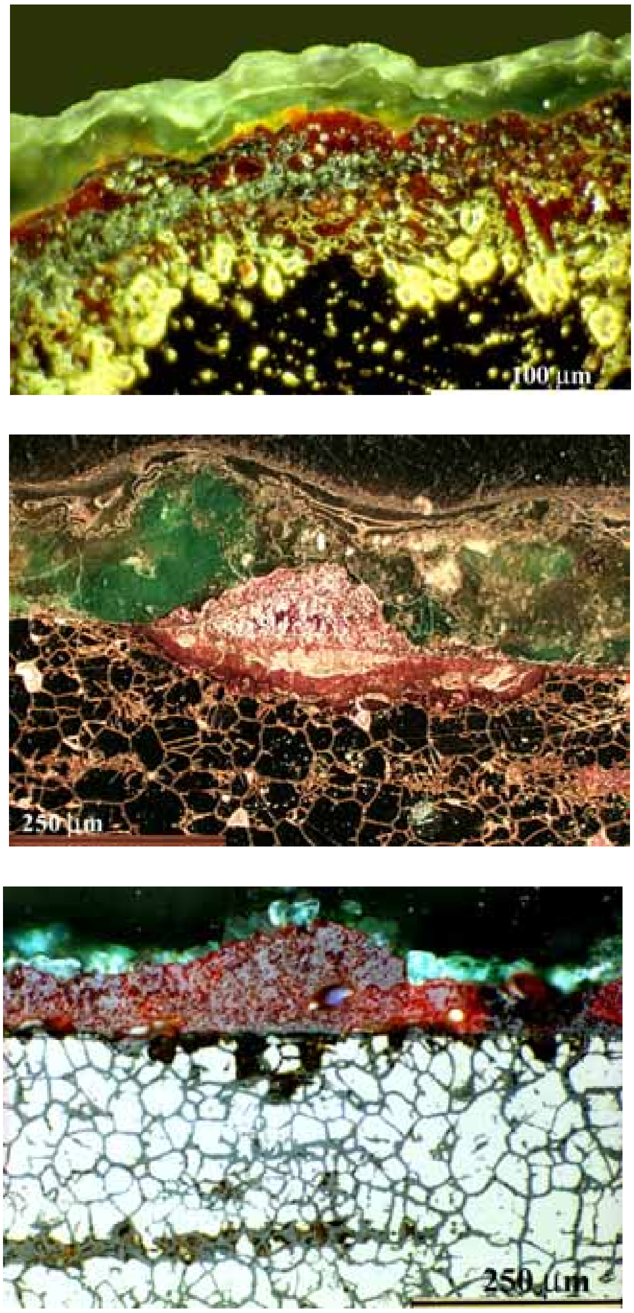
XRD has shown the presence of copper and tin species such as romarkite (SnO), cassiterite (SnO_2), cuprite (Cu_2O), tenorite (CuO), carbonates such as malachite ($Cu_2(OH)_2CO_3$), azzurrite ($Cu_3(OH)_2CO_3$), smithsonite ($ZnCO_3$), leadlhillite ($PbSO_42PbCO_3Pb(OH)_2$) and cerussite ($PbCO_3$) as well as a complex copper-iron sulphide (calcopirite, $CuFeS_2$). The presence of atacamite ($Cu_2(OH)_3Cl$), nantokite (CuCl), brochantite ($Cu_4(OH)_6(SO)_4$), calcantite ($CuSO_45H_2O$) and piromorfite ($(PbCl)Pb_4(PO_4)_3$) has been also frequently monitored. This information gives evidence that the outermost corrosion layers are formed also via the interaction between soil constituents (Cl, P, Si, Fe, Al, K, Ca, S, CO_2) and metal corrosion products mainly composed of copper whose amount on the artefact surface is often decreased by the long-term corrosion (dealloying). The presence of carbonates, chlorides, silicate, phosphate, sulphate and sulphides also enriched with Ca, K, Al and Fe demonstrate a strict interaction between soil constituents and artefacts corrosion products.

Some typical examples of corrosion product structures are shown in Fig. 4 where cross-sections of bronze archaeological artefacts found in Italy and Turkey are reported.

In particular, the images (a), (b) and (c) show the nature of the corrosion products grown during the burial of a coin, a shield and a helmet, respectively. The micrographs taken by optical microscope (dark field observation) describe the complex nature of the stratified corrosion products: the dark spheroids, grains and thick layer consist of the surviving metal, the red crystals, rounded phases, erupting nodules or layers are cuprous oxide (cuprite,Cu_2O), the green compounds are Cu (II) carbonates or oxychlorides and the yellow-orange phase is cuprous chloride present at the interface between external corrosion products and metal relict.

Furthermore, images (a) and (b) of Fig. 4 show the presence of a pocket of cuprous chloride (CuCl) underneath the patina that could induce bronze disease when chloride ions will diffuse from the surface. Indeed, when cuprous chloride is exposed to the atmospheric humidity cyclically reacts with oxygen and the water coming from the humid atmosphere thus gives rise to the formation of the greenish $2Cu_2(OH)_3Cl$ (atacamite and its polymorphs) that reacts with copper to form new cuprous chloride and water. In this way copper, chlorine, oxygen and water are converted into cuprite (Cu_2O) and atacamite ($2Cu_2(OH)_3Cl$) in a cyclic and continuous process that can disfigure the archaeological object.

Cuprous chloride is formed during the burial via the interaction between copper and Cl^- anions coming from the soil. It is worth noting that large amounts of chlorine up to 22 mg/g have been monitored in the selected archaeological areas not only in the coastal sites of Sardinia but also in archaeological contexts located very far from the sea such as the desert areas of Jordan and the mountain of Ayanis (Turkey). Indeed, in very ancient times these latter areas were salty lakes and the soil is still heavily contaminated by the presence of chlorine. The images (a) and (b) also show the protective role of the copper (II) compounds and of the cuprite (Cu_2O) layer that protects the surface, and impedes the interaction between cuprous chloride and water coming from the atmosphere, and therefore, the occurrence of the cyclic and continuous copper corrosion process. This information indicates that the conservation materials and methods must locally inhibit the dangerous presence of chlorine and that a particular care must be used to avoid the removal of the protective corrosion product layers, and the contact between cuprous chloride and water and oxygen of the atmosphere. In particular, the mechanical cleaning carried out for removing the external corrosion products, encrustations and the phases coming from the soil cannot ensure the complete removal of the corroding agents such as Cl, P and S, that could be yet present within the patina thus inducing a further degradation. Moreover, the above discussed results demonstrate that the removal of Cu (II) compounds and the cuprite (Cu_2O) layer from the surface could expose the copper chlorides present under the Cu_2O layer, thus inducing the cyclic reaction of copper corrosion and therefore, inducing the partial disfiguration of the artifact. Therefore, particular attention must be paid before and during the removal of surface encrustations and corrosion products layers in particular of cuprite in order to avoid to exposure copper chlorides to humidity and oxygen.



(a)
(b)
(c)

Figure 4: Cross-sections of bronze archaeological artefacts found at Tharros (a), Ayanis (Turkey) (b,c) with different corrosion behaviour

The role of the cuprite layer has been discussed by Lucey [13] and has been considered to be acting as an electrolytical membrane allowing the transport of anions such as Cl^- and O_2^- inward and cuprous ions outward. Indeed, the presence of copper chlorides in the archaeological artefacts indicates a noticeable transportation of chlorides from the soil trough the permeable corrosion product layers to the internal zone and remaining Cu-base matrix. The accumulation of chloride ions can be interpreted as an autocatalytic reaction that facilitates the oxidation of copper resulting also in an accumulation of chloride ions and in the formation of cuprite and cuprous chloride, as described in details by Robbiola and co-workers [5]. These considerations show that uncompleted knowledge of corrosion products and degradation mechanisms as well as inappropriate conservation materials and cleaning treatments, could not stop the degradation phenomena and are not able to ensure a long-term chemical-physical stability for the archaeological bronze objects.

In reaching these latter objectives it is fundamental to identify the degradation origin and to correctly select materials and methods able to reliably stop the degradation phenomena, and also to acquire a deep insight into their performances and mechanisms as a function of the chemical composition and metallurgical features of the artefact, as well as of the degradation mechanism. The results shown above have demonstrated that one degradation source that affect the long-term stability of the Cu-based archaeological artefacts is due to the ubiquitous and nearly constant presence of chlorine inside the corrosion layers that inducesthe cyclic copper corrosion. The other source of degradation is due to the intrinsic metallurgical features of the archaeological artefacts created during the production of the alloys and the manufacturing of the objects by repeated cycles of cold or hot mechanical work and thermal treatments. These combined treatments induce segregation phenomena along the grain boundaries of the impurities present in ancient and imperfectly refined alloys, thus inducing mechanical weakness and increasing the extent of the inter-granular corrosion phenomena. Unfortunately, for the first degradation cause, it could be possible to find reliable methods and materials to stop the troublesome role of chlorine, for the second one it is not possible to find a definitive solution but only to propose some precautions.

4 Conclusions

A large number of copper-based artefacts found in excavations in different archaeological sites of the Mediterranean basin have been investigated with respect to their chemical composition, metallurgical features and corrosion products (i.e. the patina) in order to clarify the degradation mechanisms and suggest tailored conservation methods and materials.

The results show wide variation of the chemical composition of the alloys that include all kinds of ancient Cu-based alloys such as low and high tin, and also leaded bronzes, copper and copper-iron alloys.

The examination of the alloy matrix shows largely different metallurgical features thus indicating the use of different manufacturing techniques for producing the artefacts. The results of the micro-chemical investigation of the patina show the structures and the chemical composition of the stratified corrosion layers where copper or tin depletion phenomena are commonly observed with a remarkably surface enrichment of some soil elements such as P, S, Ca, Si, Fe, Al and Cl. This information indicates the strict interaction between soil components and corrosion reactions and products. In particular, the ubiquitous and near constant presence of chlorine in the corrosion layers is observed in the patina of the archaeological Cu-based artefacts found in different contexts in Italy, Turkey, Jordan, Egypt, Spain and Tunisia. This latter occurrence is considered dangerous because it could induce a cyclic corrosion reaction of copper that could disfigure the artefact.

The micro-chemical and micro-structural results also show that another source of degradation of the bronze archaeological artefacts, are their intrinsic metallurgical features whose formation is induced during the manufacturing of the objects, carried out in ancient times by repeated cycles of cold or hot mechanical work and thermal treatments. These combined treatments induce crystallisation and segregation phenomena of the impurities along the grain boundaries and could cause mechanical weakness and increase the extent of the inter-granular corrosion phenomena.

Finally, the results of the large-scale characterisation can help to identify the present conservation state of the archaeological bronze artefacts and can lead to recommendations for selecting tailored conservation methods and materials. These latter should be able to transform, in stable phases, the dangerous copper chlorides or oxy-chlorides, to stop the copper cyclic reaction and to ensure a long life for the bronze archaeological artefacts.

4.1 European dimension

The Consortium is representative of the most important European and Mediterranean Countries for what concerns the ancient Cultural Heritage (Italy, Spain, Greece, Tunisia, Egypt, Algeria, Jordan and Turkey) and material science. Indeed, the expertise and the disciplines present in the involved Departments or Institutions includes archaeology, chemistry, physic, geology, computing and material science.

4.2 Innovation and originality

The aim of the effort of archaeologists and material scientists of the different Mediterranean Countries involved in this project had the was to develop tailored restoration and conservation methods, anchored in local actions, for archaeological Cu-based artefacts selected for their historical and economical value such as coins, weapons and artistic objects. These artefacts are characterised by largely different conservation and restoration problems often tentatively solved by applying the same methodology and the same products independently of the local realities. The foreseen strategy is based on the acquisition of the knowledge of the relationship between the environmental conditions (soil nature, previous restoration and conservation treatments, external exposure, storage history, current environmental condition) and the chemical and physical properties of the artefacts, noticeable through the microchemical structure of the *patina* in order to select the best cleaning and restoration procedures via different methods.

4.3 Impacts

This project contributes to develop to the European policies regarding Cultural Heritage and its conservation, valorisation and fruition and to increase the competitiveness of the European conservation and restoration industries by creating new jobs in a wide area and by stimulating employment growth, encouraging transnationality, innovative procedures and bottom up approaches. These aspects have to be considered taking into account the possible extension of the results to all the other classes of ancient metallic objects. As a amtetr of fact in the project innovative conservation materials and methods have been developed as corrosion inhibitors and polysiloxane barrier films deposited by PECVD, plasma enhanced chemical vapour deposition technologies.

The development of an integrated information system allowing communication, control and exchange of information within the partners and European and Mediterranean Museum and Conservation Institutions is of outstanding importance. As a matter of fact, in the Cultural heritage protection field, the European added value and the contribution to the implementation of the EU policies is expressed by validating the transferability of the conservation and restoration methods and materials developed in this project to the other European and Mediterranean Countries.

5 European project details

Acronym: EFESTUS (the Greek God of fire and metalworking, that Romans called Volcanus), Contract No. INCOMED No. ICA3-CT-2002-10030, Title of the Project: "Tailored strategies for the conservation and restoration of archaeological value Cu-based artefacts from Mediterranean Countries", Co-ordinator: Gabriel Maria INGO, Affiliation: Institute for the Study of Nanostructured Materials, National Research Council, Roma, Italy; e-mail: ingo2@mlib.cnr.it.

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Monitoring the conservation of metal objects: evaluation of a new approach

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1 Introduction

Electrochemistry provides powerful methods for the conservation of metals. It can be used to stabilize corroded metal structures from jewellery to sunken wreaks [1], to clean delicate artefacts such as silver-wrapped silken threads in a garment [2], and it provides a vehicle for the basic study of corrosion processes. One of its most attractive features in a cultural heritage context is that all of the potential applications can be thoroughly studied and evaluated before use. In this article, we describe new equipment which enables electrochemical reactions occurring in the near surface of a metal (or any conducting material) to be studied in-situ and in real time using powerful and (in this context) non-destructive X-ray methods including X-ray diffraction (XRD) [3]. Once the electrochemical process has been perfected for a particular combination of, for example, a simulant metal and its corrosion layer(s), it can be tested or deployed on real objects.

A typical electrochemical process used in conservation involves immersing the artefact in an electrolyte which is a fluid containing ions in solution (a simple example of an electrolyte is NaCl (common salt) dissolved in water). In the case of a sunken wreak, the electrolyte is already present since the wreak is under the sea.

Electrochemical techniques may be used to change the chemical nature of a corrosion product on the surface or in the bulk in order to stabilize it or convert it to a protective layer, to deposit new protective layers, to convert a corroded surface back to metal (reduction), or to deliberately produce specific corrosion products for conservation studies. A significant difference between deliberately applied electrochemical reactions, and other types of chemical process, including those which cause corrosion in the first place, is that the direction of the reaction can be controlled (oxidation or reduction) which enables a corrosion layer to be converted back to metal, for example. These, and many other possible processes, require careful evaluation before application to real artefacts.

X-ray techniques provide a powerful way of undertaking part of such an evaluation, especially if, as we describe here, they can be used to observe the changes in surface chemistry as they are happening. Different X-ray measurements can identify and characterize crystalline and amorphous reaction products, give details of atomic composition, and study ions in solution in the electrolyte. In principle, they provide a complete set of methods for characterizing the reactions – with some limitations: Most metals of interest have rough surfaces (at least on the micron scale) and are non-uniform in composition – they have a grain structure which depends on the alloy and how it was worked. On this type of surface, X-ray techniques can give information on surface layers a few microns or more in thickness, but corrosion may start with layers or discontinuous patches which are nanometres thick. For this reason we also incorporate a surface-specific and chemically sensitive analytical technique into our experiments – ultra-low energy dynamic secondary ion mass spectrometry [4]. In this way, we can study layers too thin to be observed with the X-ray tools with the limitation that the surfaces have to be removed from the electrochemistry system and placed in an ultra-high vacuum instrument for this purpose. The SIMS is beyond the scope of this article, but we mention it to show that one needs quite a large range of techniques to adequately investigate this type of problem.

In order to carry out experiments of the type we describe here, one needs a very special source of X-rays. It must be intense, stable, and, for some experiments, scanable in frequency ("colour" of the X-rays). A synchrotron light source has exactly the right characteristics, so the experiments are carried out in one of several synchrotrons around the EU.

2 Electrochemistry and the cell

In an electrochemical cell designed for quantitative electrochemistry there are usually three electrodes (Figure 1). One of these (the working electrode) is made of the metal(s) of interest (and will, where the technique is used directly, be the artefact which needs cleaning or protecting). Then there is an electrode which acts as the source of current for the cell – the counter electrode. This is often made of a material which is unreactive such as platinum. The cell current then flows between the counter electrode and the working electrode, through the electrolyte. The size of the current (for a given electrode area) tells us about the strength of a reaction, whilst its direction determines whether the reaction is reducing (e.g. cleaning) or oxidising (e.g. corroding or coating). The third electrode is the reference electrode. The potential difference between this and the working electrode is either measured in order to help identify exactly which reaction is taking place, or set in order to promote specific reactions. The reference electrode is a miniature electrochemical cell in its own right – one which generates an accurately known "reference potential", in comparison with which the potential on the working electrode can be measured. The currents and voltages are controlled or measured by an electronic device called a potentiostat, these days driven by the user through a PC.

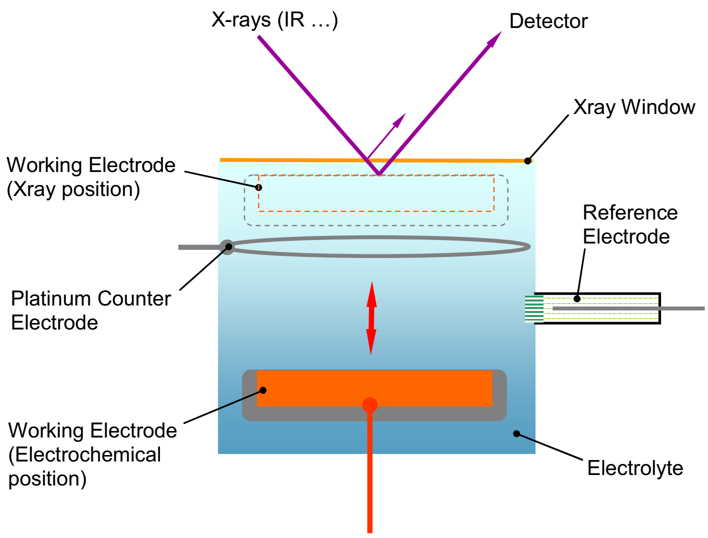

Figure 1: Schema of an electrochemical cell suitable for spectroelectrochemistry. This juxtaposition of the incident and exit beams, the window and the sample surface is known as the Bragg configuration. Note that the working electrode may be moved if necessary, so that it is properly immersed in the electrolyte (electrochemical position) or close to the window (X-ray position) in order to minimize adsorption and scattering of the X-rays.

The electrolyte is a liquid which conducts electricity (one example would be tap water). It is usually a solution of an acid, a base, or a salt in water, although other solvents are possible. The solute is chosen according to the reactions one wishes to study or promote. The dissolved substance splits into equal numbers of positive and negative ions in solution, and if, for example, the negative ions react with the working electrode, the resulting localization of charge gives rise to a potential difference which is characteristic of the reaction. Alternatively, the external application of this potential can force the reaction to take place.

In practice, the measured (or applied) potential may not identify or create a reaction uniquely, and, in any case, the chemistry of real corrosion layers is complex. If one can observe the reacting surface (and the electrolyte in which it is immersed) with a spectroscopic technique at the same time as making the electrochemical measurements (or when driving the cell in a particular way) a huge amount of extra information specific to the system can be obtained, ambiguities can be resolved, and the relationships between the electrochemical parameters and the sample chemistry can be accurately established. In principle, this allows one to move on to calibrating inexpensive electrochemically based sensors for monitoring artefact in storage, for example.

3 X-ray diffraction

Why use X-rays? For our purposes, they have a very important property – they interact directly with the atoms of a material in a way which allows atomic composition, and molecular structure to be determined.

If the atoms are regularly arranged in space, as they are in a crystalline material, then an incident beam of X-rays will be scattered off in a number of well defined directions which are directly related to the spacing between the planes of atoms in the crystal. The principle is similar to the one which gives rise to the rainbow colours observed from a thin oil film on water illuminated by white light. In that case, different thicknesses of oil pick out and scatter different colours from the light into the eye. From observations of colour at different angles you could calculate the thickness of the oil film. (The key difference is that X-rays have a wavelength comparable to interatomic distances (~0.5 nm), whereas visible light has a wavelength comparable to the thickness of an oil film (~0.5 μm).) A plot of the scattered X-ray intensity against the scattering angle in one or two dimensions is known as a diffraction pattern. A single crystalline substance has a unique diffraction pattern, and can, in principle, be identified from it (see next section). Mixtures of materials give rise to a diffraction pattern which is (sometimes only approximately) the sum of that from each individual substance. In this work, we are concerned with one-dimensional diffraction patterns, known as line spectra. Provided enough lines can be resolved (separated), mixtures of crystalline substances can be identified with confidence, and one obtains molecular or structural information.

4 Combining the cell and X-ray diffraction

We need to be able to analyse surfaces in the electrolyte whilst they are undergoing the electrochemical processing. At high energies (100 keV and above), X-rays will, for example, penetrate several centimetres of water, but be significantly absorbed by solid materials – this is the basis of medical radiography. However, at energies useful to us, X-rays will penetrate only a few hundred microns of fluid, and the beam becomes become progressively more scattered and attenuated as the thickness is increased. Because the X-rays have to interact with the sample surface, they have to traverse any electrolyte over the sample twice – once on the way in, and once on the way out (Figure 1). For X-ray analysis, therefore, we need to keep the electrolyte thickness down to below 200 μm. On the other hand, this provides a rather restricted access to the electrochemical process, and runs the risk of contaminants building up over the surface, and also of restricting the current flow to the edges of the sample. Indeed, one of our initial experiments (described below) may have suffered from this limitation. We have therefore designed a cell where the working electrode can be moved to the X-ray window for analysis, and withdrawn into the electrolyte to ensure an undistorted electrochemical process. This is done under computer control, and the electrochemistry and X-ray analysis are fully automated.

The cell is shown in Figure 2. The X-rays enter through an 8 μm thick Kapton™ window which seals the top of a polychlorotrifluroethylene (PCTFE) cup containing the electrodes and electrolyte. The cell is basically of the Bragg type (Nagy and You 2002) and is designed for use with working electrodes which may be rectangular or circular, and up to 16 mm across in their largest dimension. It is therefore suitable for use on beamlines with footprints from the sub-micron to the millimetre scale. The overall dimensions are 100 mm high by 60 mm outside diameter. The bore of the cell is around 30 mm. The cell may be mounted in any orientation.

PCTFE was used for the large parts of the cell such as the body and the piston (supporting the working electrode) because of its overall excellent chemical resistance and its relative hardness and dimensional stability around room temperature in comparison with the alternative polytetrafluoroethylene (PTFE). External feedthroughs for wire and liquid use HPLC fittings (Upchurch Scientific Inc.) or a custom design with Viton® O-Ring seals.

The working electrode is moved using a rotary stepper motor driving a cam through a dynamic seal. A second linear stepper motor drives a small syringe which controls the cell volume, and which can therefore be used to adjust the curvature of the Kapton window giving fine control over the thickness of the fluid pocket over the working electrode.

The counter-electrode is made from 1 mm diameter Pt wire, and the reference electrode is a custom designed Ag/AgCl type with a Vycor® porous tip ~3.2 mm diameter (Bioanalytical systems Inc.).

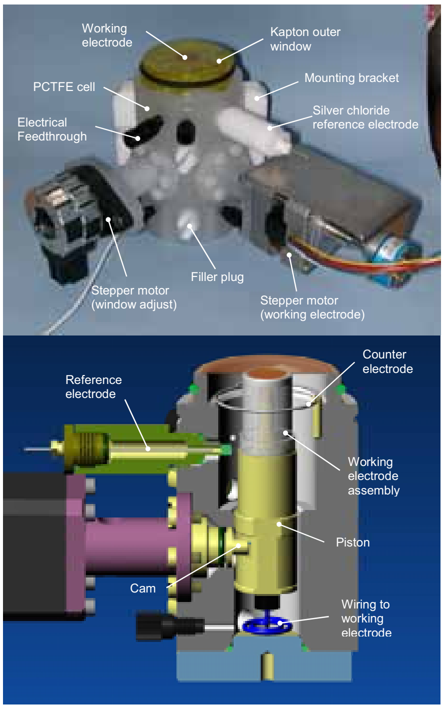

Figure 2: Photograph of the cell with a sectional view showing the piston and working electrode assembly

5 Applications

As a practical example of using the electrochemical cell, we examine how corrosion potential (Ecorr) measurements can contribute to providing information on the effectiveness of storage and stabilisation treatments of copper objects [5-6].

Archaeological copper-based artefacts recovered from wet and salty environments, should not be exposed directly to the atmosphere as the metal usually corrodes at an accelerated rate in the oxygen-rich air [7]. These objects are typically stored in tap water and stabilized in sodium sesquicarbonate solutions [8-10]. Nevertheless previous studies have shown that corrosion layers are transformed during these processes and provoke side effects such as the modification of the natural patina [11-12] and the development of new active corrosion. The latter implies the need for continuous monitoring. Present monitoring methods involve the analysis of the chloride concentration in solution. When this concentration exceeds a predetermined value, the solution is changed for a fresh batch. This procedure is repeated until the chloride concentration remains low enough. The disadvantage of this method is the fact that it is an indirect monitoring method: the conservator has no idea what is happening with the metal surface. Hence a different monitoring method is needed and this is where Ecorr measurements may have a role to play.

Ecorr measurements are based on the measurement of the corrosion potential (open circuit potential) of the metal object against a stable reference electrode. The potential obtained depends on the solution (electrolyte) in which the object is immersed (which is known as it was chosen by the conservator) and the composition of the metal or its corrosion products in case corroded. The hypothesis is that stable Ecorr data imply a stable surface chemistry.

Experiments in this study were carried out on simulated materials. Five corrosion products commonly found on real copper artefacts were considered. Cuprite (Cu_2O) is regularly found on copper artefacts and is a stable product [7, 13]. Within the copper chlorides nantokite (CuCl), atacamite and paratacamite (both isomers of $Cu_2(OH)_3Cl$) were selected. Nantokite is considered as the main catalytic agent for active corrosion. The presence of this cuprous chloride as a corrosion product adjacent to the metallic surface can create long-term problems for the stability of an object. Bronze disease or pitting corrosion is usually attributed to this corrosion product [7]. Atacamite and paratacamite are two other important chlorides in bronze corrosion. They are often considered as end products and are formed on top of the active corrosion areas. Atacamite is the most common of the $Cu_2(OH)_3Cl$ isomers, but often alters into paratacamite [7, 13]. Chalcocite (Cu_2S) is typical of marine artefacts found in anaerobic environments [7]. In what follows the experiment will be elaborated taking nantokite as an example.

Prior to an experiment or to the corrosion simulation, pure copper coupons (ADVENT, purity 99.9%) were ground on 1200 grit SiC paper to obtain a fresh surface. To smooth the surface further, they were polished on a cloth covered with alumina powder of 1 µm particle size. Most of the adhering Al_2O_3 particles were removed by rinsing the surface thoroughly with deionised water and cleaning the coupon in an ultrasonic bath (but see [4]). Copper covered with nantokite (CuCl) was obtained by immersing pure copper coupons for one hour in a saturated $CuCl_2.2H_2O$ solution. After rinsing with deionised water they were exposed to the air for a night [14]. Figure 3 shows a photograph of a corroded copper coupon.

The coupons were immersed in a sodium sesquicarbonate solution in order to imitate the stabilization treatment. Various concentrations of sodium sesquicarbonate solutions are used by conservators to stabilize bronze artefacts. However lower concentrations are favoured though to limit rinsing steps. For this study a 1 wt% sodium sesquicarbonate solution was prepared by dissolving 11.89 g/L of $Na_2CO_3.NaHCO_3.2H_2O$ (Sigma) in deionised water (pH = 10).

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The Ecorr measurements were performed using a CHI1232 hand held potentiostat (IJ Cambria Scientific Ltd) connected to a laptop. A silver / silver chloride electrode (SSCE, Ag/AgCl/KCl (3 M)) was used as reference electrode (= 0.440 V vs. NHE). The prepared coupon disc electrodes were analyzed in 30 mL of electrolyte solution. No stirring was applied. Simultaneous synchrotron X-ray diffraction (SR-XRD) experiments were carried out at station 2.3 of the Synchrotron Radiation Source, Daresbury Laboratory (UK). A parallel monochromatic beam with a wavelength of 1.6 Å was used to analyze the sample surface. Parameters were chosen such that the incident beam angle at the cell surface was fixed at 10º and that an area at the cell surface of 2 mm^2 was analyzed.

Figure 3: Corroded copper electrode. The corrosion product is mostly nantokite

In previous measurements we attempted to obtain the correlation between the surface behaviour of nantokite in a 1 wt% sodium sesquicarbonate solution (0.05 M $NaHCO_3.Na_2CO_3$) and Ecorr data using "ex-situ" SR-XRD measurements as a function of time [15-16]. The measurements in this case were done by removing the samples from their solution at regular intervals and performing SR-XRD measurements on a small sample of powder scratched from the surface. Results showed that nantokite (CuCl) transforms into cuprite (Cu_2O) over a period of a few hours. Ex situ measurements, however, result in the need for several duplicate samples. The surface composition is likely to change when exposed to air and the sample can as result not be re-used in the Ecorr experiment after XRD analysis. In this study, the fact that Ecorr and SR-XRD analyses can be done simultaneously in-situ, avoids the problem. Not only does the sample not need to be removed from the solution, but also more XRD data per sample can be acquired within a specific time frame.

Figure 4 shows a typical SR-XRD profile of a copper sample covered with nantokite and some cuprite, while Figure 5 shows the variation of the SR-XRD peak heights of nantokite and cuprite as a function of time.

Each SR-XRD scan lasted 31 minutes. The peak height of each individual measurement is plotted at the middle of each measuring period. The SR-XRD results clearly show the disappearance of nantokite as a function of time. In fact, after 120 minutes of immersion, the nantokite signal has disappeared into the background noise due to scattering in the fluid. The cuprite signal, on the other hand, grows by more than a factor of 3.5 over this time, from a small level due to the presence of some cuprite on the sample prior to immersion into the sodium sesquicarbonate solution. This is in agreement with the theory of Oddy and Hughes [8], which predicts that nantokite can react with water to form cuprite through the following reaction:

$$2CuCl + H_2O \leftrightharpoons Cu_2O + 2Cl^- + 2H^+$$

According to the same authors nantokite can also be transformed into paratacamite. Previous ex-situ experiments, in which the electrode was removed after one day of immersion and measured a few days later using SR-XRD, were able to confirm this [15-16]. Further investigation, however, is needed to detect whether the formation of paratacamite actually takes place after more than three hours of immersion or whether it is formed due to contact with the atmosphere when the sample is taken out of its solution.

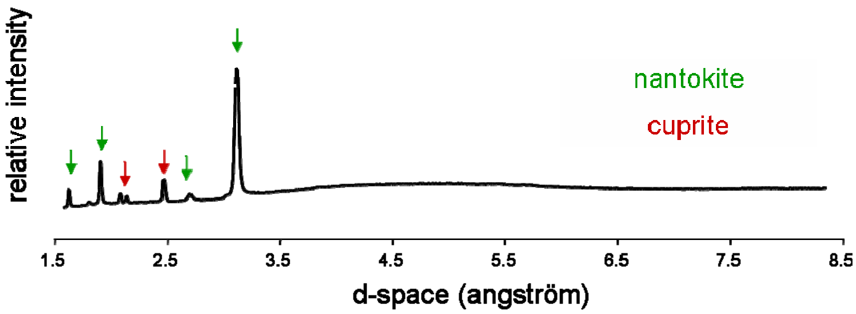

Figure 4: XRD spectrum of corrosion products scraped off the electrode showing the presence of nantokite and cuprite

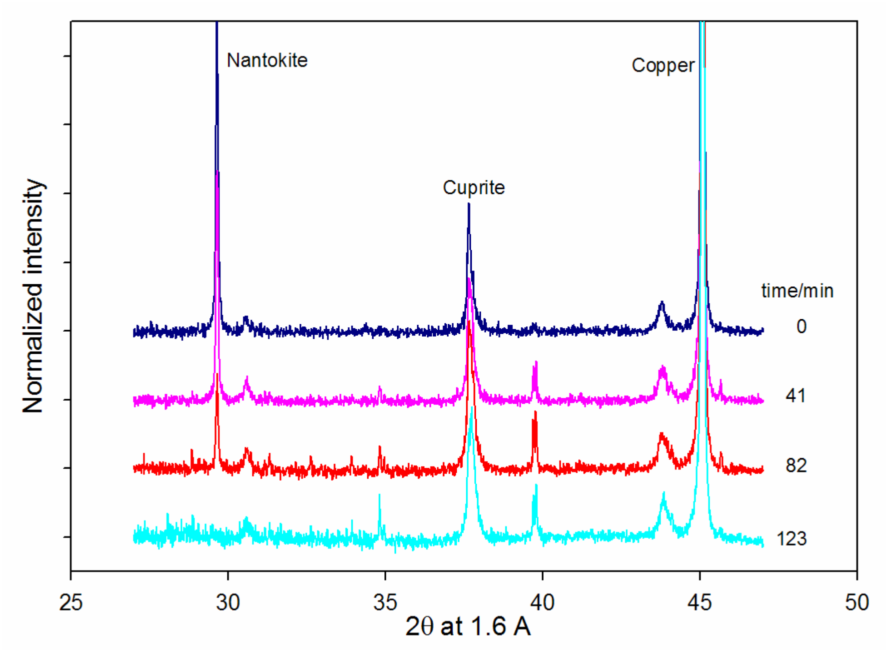

Figure 5: Time-resolved XRD spectra taken during the conversion of nantokite to cuprite in sodium sesquicarbonate

Figure 6 shows the corrosion potential versus time plot corresponding to the data in Figure 5. The x-axis shows the immersion time (the vertical grey lines indicate the start of each SR-XRD measurement). The y-axis gives the corrosion potential in Volts versus the Ag/AgCl/KCl (3 M) reference electrode.

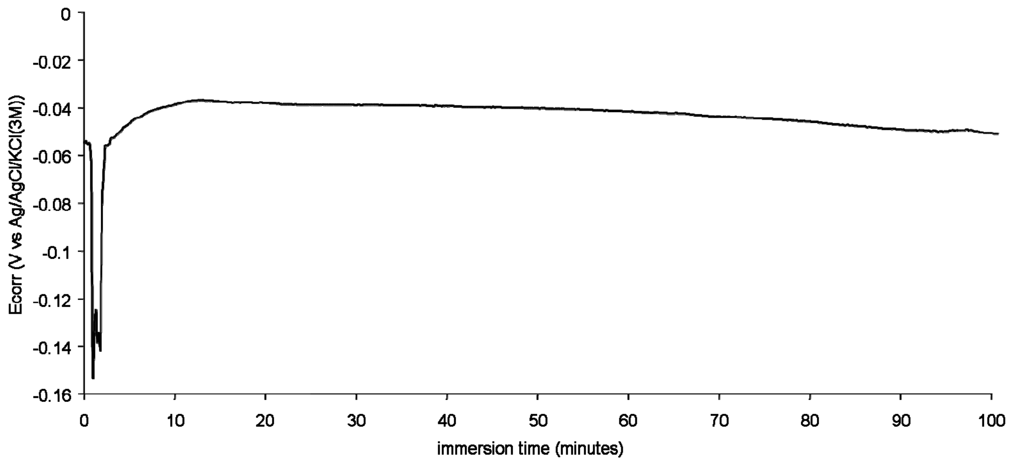

Figure 6: The corrosion potential versus time plot corresponding to the data in Figure 5. The x-axis shows the immersion time (the vertical grey lines indicate the start of each SR-XRD measurement). The y-axis gives the corrosion potential in volts versus the Ag/AgCl/KCl (3 M) reference electrode.

The variation of the corrosion potential with time recorded in the in-situ cell looks very similar to results obtained using a standard electrochemical cell. The limited thickness of the fluid layer (175 µm) seems to have no significant effect on the transformation of nantokite in sodium sesquicarbonate. Nevertheless, when comparing the SR-XRD results with the Ecorr data, the hypothesis that a stable Ecorr means a stable surface is not supported. A significant decrease in the amount of nantokite might be expected during the first 30 minutes since the corrosion potential shows a large alteration. In between 30 and 120 minutes of immersion the corrosion potential is more or less stable, implying, according to the hypothesis, no change in the surface composition. The SR-XRD data, however, tell a different story in that nantokite continues to decrease for at least 120 minutes. A possible explanation could be the inhomogeneity of the surface composition. Different areas on the surface can have more (or less) nantokite in their corrosion layer than the surrounding material. The time taken for the nantokite to disappear will then vary from place to place. Whereas the corrosion potentials measured give an average value over the whole surface, the SR-XRD measurements are performed on a smaller area. If it is the case that the corrosion potential stabilises too early, whilst there are still pockets of corrosion on the artefact, then its use in a sensor would be problematic. Further experiments are required to clarify this.

6 Summary and conclusions

Synchrotron-based X-ray techniques can be used to observe and characterise electrochemical corrosion and cleaning processes as they are happening inside the electrochemical cell. They therefore allow conservation and storage measures to be evaluated on simulated or real materials, either for the calibration of inexpensive sensing systems, or to evaluate the processes themselves.

We have developed an electrochemical cell which is engineered so as to permit X-rays from a synchrotron beamline to be scattered or absorbed by the surface of a sample whilst electrochemical reactions are taking place. X-rays emitted from the surface then carry time-resolved information on the specific reactions as they occur. During the analysis, the surface can remain immersed in electrolyte or exposed to air so as to study the process in the most relevant way, and electrochemical data can be measured coincidentally. Although similar in-situ cells for the study of idealized (e.g. atomically flat, single crystal) surfaces have been described, this is, so far as we are aware, the first time such experiments have been done on rough (at least on the micron scale), polycrystalline, impure metals typical of real artefacts.

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