SPECTROSCOPIC IMAGING AND CHEMOMETRICS

For the characterization of materials of artistic and cultural interest

Proceedings of the Workshop (Matera Campus, UniBas, 15-16 december 2022)

edited by Anna Maria Salvi,
Graziella Bernardo, Antonella Guida

BUP
Basilicata University Press

Miscellaneous

Spectroscopic imaging and Chemometrics

For the characterization of materials of artistic and cultural interest

Proceedings of the Workshop (Matera Campus, UniBas, 15-16 december 2022)

edited by
Anna Maria Salvi, Graziella Bernardo, Antonella Guida

BUP
Basilicata University Press

Le relazioni scientifiche di questo volume sono state curate e sottoposte a doppia valutazione anonima secondo i requisiti redazionali della BUP / The scientific reports in this volume have been edited and subjected to anonymous double evaluation according to the editorial requirements of the BUP.

Progetto grafico e impaginazione: Oltrepagina, Verona
Immagine di copertina: https://dicem.unibas.it/site/home/dipartimento.html (Campus Via Lanera 20, 75100 Matera)

Università degli Studi della Basilicata
Biblioteca Centrale di Ateneo
via Nazario Sauro 85
I - 85100 Potenza
https://bup.unibas.it

ISBN 978-88-31309-21-9
Published in Italy
Prima edizione: luglio 2023

Index

SCIENTIFIC CONTRIBUTIONS FOR CULTURAL HERITAGE

CHEMOMETRIC LESSONS

INNOVATIVE EQUIPMENT

Preface

Multidisciplinary Investigation and Multivariate Analysis for Cultural Heritage

The two days of the Christmas Workshop, held on 15 and 16 December 2022 at the Matera University Campus, as detailed in the program available in the Appendix, successfully ended with the BUP publication of this Volume. The event is part of the celebratory year for the fortieth anniversary of the University of Basilicata (UniBas 1982-2022). The support and patronage of the rectorate of the University of Basilicata and the Department of European and Mediterranean Cultures: Architecture, Environment, Cultural Heritage (*DiCEM*) in Matera and the Department of Science (*DiS*) in Potenza with the involvement also of the administrative staff for the management of the event, is sincerely acknowledged.

The *Reports* section of the Volume exemplifies, in the form of divulgation contributes, the collaborative research and study interests of UniBas, CNR, and other research institutions/industries operative in Basilicata and its surroundings. The published reports deal with thematic that enter the objectives of research projects dedicated to the conservation and planned and predictive maintenance of cultural heritage. The book testifies the efforts made by researchers at the University of Basilicata in adopting the methodological approach to conservation that requires dialogue and synergetic cooperation between different disciplines, too surreptitiously categorised into the humanities and sciences. The book also aims to raise awareness of the importance of diagnostics, the integrated use of spectral techniques, and the crucial role of specialist skills in data interpretation. An analytical datum is nothing more than a datum. It becomes a result after a not-always-easy job of understanding and validation. The location of the chemometric Workshop in Matera was not accidental. The city has been the European capital of culture in 2019. It has a remarkable architectural heritage with the peculiar coexistence of excavated and built structures. The millennial history of the city with settlements of prehistoric times is due to the calcarenite rock of the geographical area. The old town, called Sassi, and the Archaeological Park of the Rock Churches belong to the UNESCO World Heritage since 1993. The complexity and variety of the urban ecosystem with built heritage of remarkable historical and artistic value make the city an open laboratory of experimentation.

The opening of the Workshop with scientific reports, preceding the interactive lessons and laboratory exercises of the chemometric course, helped to illustrate multidisciplinary research and innovative applications in the BB.CC area and also to demonstrate, in due cases, the need for statically advanced methodologies to extract the maximum information from the experimental data.

The 'heart' of the Workshop is represented in the Volume by the *Chemometrics lessons* section contributed by the expert teachers (UniGE and UniBO) who oversaw the chemometrics course over the two days intending to stimulate the participants' interest in the 'multivariate analysis' with computer-guided exercises on 'case studies' concerning the characterization of materials of artistic and cultural interest, with particular reference to spectroscopic imaging.

In parallel, the Pra.Ma. Workstation was of fundamental importance during the Workshop, demonstrating the techniques used to characterize materials and advanced instrumentation released by SPECS and other manufacturing companies the group represents in Italy. As summarized in the introductory page of the '*Innovative equipment*' section, the general information from Pra.Ma. group is followed by a specific note by SPECS on EnviroEsca, the newly released XPS instrumentation operative at near-ambient pressure.

As reported in the final relation of the event to the University, thanks to the organizing committee and support of the Pra.Ma. group and UniGE, the primary aim of the Workshop to promote knowledge of multivariate analysis methodologies was achieved, considering the high number of participants registered (in person and online) to whom downloading of the dedicated software, used during the computer exercises for data processing, was allowed. At the same time, the dissemination of research topics on cultural heritage, the functioning of instruments in use, and new technological releases were also promoted.

Finally, based on the success of the Workshop, the re-proposition of more extensive workshops and 'chemometrics schools' was announced to complete the formation of 'expert' researchers who can then be able to give chemometrics lessons, thus contributing to expanding the didactic offer of the University.

Anna Maria Salvi
Graziella Bernardo
Antonella Guida

Introduction

The care of cultural heritage: reports of experimental studies and development of databases

The institutional greetings from representatives of DiCEM and DiS departments opened the Workshop and welcomed the participants. Prof. Antonella Guida, prof. Sabino A. Bufo (UniBas) and Dr. Fausto Villani (TAB Consulting S.r.l.-Potenza) introduced the morning session by giving an excursus of the scheduled talks.

The Workshop was an opportunity to present the results obtained by the partners resident in the Basilicata Region within the project "Product and process innovation for sustainable and planned maintenance, conservation and restoration of cultural heritage – SCN-0520)", financed with European funds through the program "Smart Cities and Communities and Social Innovation" of the Italian Ministry of University and Research (MUR).

The presentations relating to the SCN macro-objectives, concerned:

- The diagnostics phase through characterization of the various forms of degradation and biodegradation of stone materials, using advanced techniques and multidisciplinary approaches.
- Study and develop new effective products with low environmental impact and cost for restoring degraded stone materials of cultural heritage. Bio-remediation based on natural "organic" biocides and Bio-restructuring using microorganisms capable of depositing reconstructive minerals.
- Definition of procedural and operational models for implementing a maintenance system. The performance of actions for the sustainable management of cultural heritage, also through developing a technological platform for preventive interventions and scheduled maintenance.

Additional presentations given by researchers from the Basilicata Region, not directly included in the Smart Cities project, have enriched the Workshop by expanding the experimental applications and providing significant scientific contributions to the topic of safeguarding cultural heritage with case studies related to the characterization of artistic-cultural materials of different nature, using combined methodologies and innovative instrumentation.

The first communication centered nicely on the objective described in the final report of Project Smart Cities. Dr. Vito D. Porcari (UniBas) gave a scientific talk about "The maintenance of cultural heritage: actions and strategies of a planned process for enhancing the architectural heritage". Lithic artworks such as churches, historical buildings, and every usage object are our precious cultural heritage, the memory of our history step needed to build the present and future. These artistic heritages with morphological, chemical, and physical properties are dissimilar, making them a "unicum" characterized by a specific vulnerability. Their decay is unavoidable, but it is challenging for humankind to protect and preserve them.

Dr. Paola Di Leo (IMAA-CNR, UniBas) underlined the necessity of specific analytical activities for artifact characterization. She depicted an advanced methodology addressed to the study of archaeological finds attested at the 14th and 15th centuries with a presentation titled "Micro X-ray fluorescence imaging and chemical-mineralogical characterization of pigments in materials of artistic-cultural interest".

Dr. Graziella Bernardo (UniBas) focused on "Green materials and non-invasive diagnostic methods for the sustainable conservation of architectural heritage". The research activities allowed the characterization of calcarenite and the identification of degradation of the three case studies of San Pietro Barisano, San Francesco d'Assisi, and Santa Lucia alle Malve, chosen as representative examples of the vulnerable architectural heritage of the city of Matera. Using non-invasive and cost-effective diagnostics also enabled the comparative verification of medium and long-term effectiveness of aqueous formulations developed by the industrial partner Icap Leather and some commonly used consolidating and protective commercial products.

Dr. Carmine Schiavone (TAB Consulting S.r.l.): opened a new chapter by presenting "He-Main", an information platform for managing and maintaining cultural heritage. He-MaIn is a process innovation that, along with research and development of new formulations for the restoration of artworks, aims to manage available resources and cultural policies by creating a technological platform for the preventive scheduling of maintenance interventions. Synergistic and multidisciplinary actions resulted from the contemporary adoption of ICT technologies and chemical, architectural, and biotechnological knowledge.

Prof. Angela De Bonis (UniBas) returned to analytical application techniques with an invited lecture about "Laser spectroscopes for Cultural Heritage: characterization of metallic and stone materials". She focused on describing the most recently developed laser spectroscopy technique (Laser Induced Breakdown Spectroscopy (LIBS)). She showed how the combined use of LIBS and micro-Raman spectroscopy could provide a detailed characterization of the elemental and molecular composition of the corrosion patina of bronze artifacts.

Dr. Giovanna Rizzo and Dr. Roberto Buccione (UniBas) jointly addressed the "Petrographic, mineralogical and geochemical approach applied to Cultural Heritage". The case study concerned the multi-analytical characterization of 16 samples of mortars representative of a medieval settlement (Satrianum Pz) to identify the raw materials used and their origin.

A well-focused communication was given by Prof. Laura Scrano (UniBas), who presented a theme central to the Smart Cities Project, "BIO-Innovative strategies for the 'cleaning' and 'restoration' of stone and metal heritage". For the cleaning of these materials and to contribute to the protection of the environment and health, she tested extracts of spontaneous plants such as *Solanum nigrum* L. and *Moricandia arvensis* L., together with secondary metabolites obtained from a culture of the fungus *Beauveria bassiana* Will. All the tested products showed high efficacy at low concentrations and have proven harmless from an environmental and toxicological point of view.

Dr. Nicola Cardellicchio (UniBas) gave an invited lecture on "The impact of climate change on Cultural Heritage". He summarized the environmental stressors that can modify the physical, chemical, and biological conditions, affecting the composition of the materials used in cultural artworks. Climate changes alter the water cycle, the acidity of the atmosphere, and the frequency and intensity of extreme events such as drought, floods, landslides, and sea levels. All these factors have inevitable repercussions on cultural heritage. Studying forecasting models is, therefore, essential for adopting mitigation and safeguarding policies.

Dr. Francesco Cardellicchio (IMAA-CNR) took the floor and presented an extensive report on the "Use of surface analysis techniques for diagnosing cultural heritage degradation". He focused on the degradation of the internal surfaces of the church "San Pietro Barisano", Matera's most important rock church. Since the church was excavated in the calcarenite rock, the research was mainly directed to the study of the degradation of the stone material in the presence of extensive phenomena of biological contamination of the surfaces. The main diagnostic contribution was provided by XPS (X-ray Photoelectron Spectroscopy), which has proven to be helpful for the possibility of analyzing small quantities of dust samples, and for the rapidity of the analysis, which does not involve particular treatments of the sample.

On the whole, the scientific reports propose new solutions for the care of cultural heritage through (i) the complete classification of artifacts; (ii) monitoring of environmental parameters; (iii) the use of analysis tools (spectroscopic, chemometric, etc.); and (iv) managing of maintenance and restoration activities, as detailed in the Reports collection of this Proceedings Book.

The necessity of data-driven approaches, supported by a digital platform, was demonstrated together with chemometric analysis to extract the maximum information from experimental measurements. The need to deepen the chemometric methods in the field of Cultural Heritage and the use of advanced instrumentation was fulfilled by the chemometric lessons and contributions of the subsequent sessions, primarily representative of the Christmas workshop, well summarized in the second half of the Book.

Sabino Bufo
Antonella Guida
Fausto Villani

SCIENTIFIC CONTRIBUTIONS FOR CULTURAL HERITAGE

Graziella Bernardo
Department of European and Mediterranean Cultures (DiCEM)
University of Basilicata, Matera, Italy

Diagnostics for sustainable conservation of building heritage

Abstract

The contribution summarizes some diagnostic activities on the religious architectural heritage of the Sassi and the Park of the Rupestrian Churches of Matera, UNESCO World Heritage Sites since 1993, performed within the national research project 'Product and process innovation for planned and preventive maintenance, preservation and restoration of cultural heritage" funded by the Ministry of University and Research in the Smart Cities and Social Innovation program. The research activities have been carried out through the integrated use of laboratory analytical techniques and on-site diagnostic techniques. The experimental activities have been carried out with a multidisciplinary approach in cooperation with the Superintendency of Archaeological and Landscape Heritage of Basilicata, industrial partners, market companies of restoration products and restoration work companies. The activities allowed the characterization of calcarenites and the identification of degradation of the three case studies of San Pietro Barisano, San Francesco d'Assisi and Santa Lucia alle Malve, chosen as representative cases of the vulnerable architectural heritage of the city of Matera. The use of non-invasive and cost-effective diagnostics also enabled the comparative verification of medium and long-term effectiveness between innovative acrylic-urethane resins in aqueous solvent developed by the industrial partner Icap Leather and commonly used consolidating and protective commercial products.

Keywords

Calcarenites; preservation of building surfaces; pilot products; laboratory analytical technique; on site diagnostic techniques.

Riassunto

Il contributo descrive le attività diagnostiche condotte sul patrimonio architettonico religioso dei Sassi e del Parco delle Chiese Rupestri di Matera, Patrimonio dell'Umanità UNESCO dal 1993, svolte nell'ambito del progetto di ricerca nazionale "Innovazione di prodotto e di processo per la manutenzione programmata e preventiva, la conservazione e il restauro dei beni culturali" finanziato dal Ministero dell'Università e della Ricerca nell'ambito del programma Smart Cities and Social Innovation. Le attività di ricerca sono state condotte attraverso l'utilizzo integrato di tecniche analitiche di laboratorio e di tecniche diagnostiche in situ. Le attività sperimentali sono state condotte con un approccio multidisciplinare in collaborazione con la Soprintendenza per i Beni Archeologici e Paesaggistici della Basilicata, partner industriali, aziende del mercato dei prodotti per il restauro e imprese di restauro. Le attività hanno permesso la caratterizzazione delle calcareniti e l'identificazione del degrado dei tre casi studio di San Pietro Barisano, San Francesco d'Assisi e Santa Lucia alle Malve, scelti come casi rappresentativi del patrimonio architettonico vulnerabile della città di Matera. L'utilizzo di una diagnostica non invasiva ed economicamente vantaggiosa ha permesso anche di verificare la comparazione dell'efficacia a medio e lungo termine tra le innovative resine acrilico-uretaniche in solvente acquoso sviluppate dal partner industriale Icap Leather e i prodotti commerciali consolidanti e protettivi comunemente utilizzati.

Parole chiave

Calcareniti; conservazione di superfici edilizie; prodotti pilota; tecnica analitica di laboratorio; tecniche diagnostiche in loco.

1. Introduction

The conservation of cultural heritage is a complex challenge that requires multidisciplinary teamwork with an effective synergetic capacity for sharing knowledge with each other and between all the stakeholders (owners of the property, preservation bodies, restoration companies, suppliers of materials and technologies). However, despite the widespread awareness of the need for a multidisciplinary approach to conservation science, there is still a certain difficulty to carry out teamwork and, of course, achieving the overriding objective of preserving cultural heritage. Moreover, although the Code of Cultural Heritage and Landscape defines conservation as a coherent and planned activities of study, prevention, maintenance, and restoration, most of the actions of the conservation process involve the recovery and/or restoration of the severely damaged building heritage.

Diagnostics, i.e. the set of analysis methods and techniques, plays a crucial role in the current heritage conservation strategies focused on preventive and planned maintenance. Nevertheless, they are still too often considered as a mere regulatory requirement in the ordinary design of interventions for the recovery and valorisation of building heritage. In addition, many laboratory techniques are unfairly categorized as invasive investigations as they require an on-site sampling phase that is not easily granted by property protection bodies.

2. The building heritage of the city of Matera

The city of Matera has a remarkable building heritage listed in the UNESCO World Heritage since 1993. It includes the ancient part of the city named Sassi and the surrounding area of the Park of Rupestrian churches. The main characteristic of Matera's building heritage is the co-existence of built and dug structures with continuous stratifications and change of use throughout the thousand-year history of the city.

As in most cities in the Mediterranean area, the typical building material is calcarenite, a sedimentary rock of biochemical origin with a low degree of alteration in which fossil shells and skeletons of marine organisms can still be discerned (Fig. 1). The calcarenite of Matera belongs to the carbonate stratigraphic unit of the infra-Pleistocene deposits of the Fossa Bradanica called Calcarenite of Gravina (Pieri et al, 1996; Tropeano & Schiattarella, 2019).

Calcarenites are highly friable, easily quarrying and processing in ashlar for masonry, flagstone for paving and ornamental building components with different and complex forms. Unfortunately, these limestone rocks are highly vulnerable to various forms of chemical, physical and biological degradation (Bernardo & Guida, 2015).

Calcarenite has a great variability of compositional and micro-structural characteristics depending on the size of grains and on the type and quantity of the matrix and of the cement. Consequently, their technological properties and durability have a high variability as well. Typically, they have a low mechanical strength, a high open porosity, and a poor durability (Andriani & Walsh, 2002).

The severity of alteration and degradation of calcarenites depends on their microstructural characteristics. It is not uncommon indeed to observe contiguous ashlars in the same masonry with varying degrees of alveolization (Fig. 2). In addition, the high variability of the microstructural characteristics of calcarenites also affects the behavior of the materials used as consolidating and protective agents.

Figure 1. Fossil shells in the upper part of the rocky outcropnear to the entrance of the church of San Pietro Barisano.

The original matrix of the town is the open cave, carved obliquely into the rock to exploit the solar radiation as a passive system and obtain an adequate level of comfort year-round.

The open cave has been evolved towards the cave buffered by a façade in masonry with an opening for the entrance door and an overhead light to ventilate and illuminate the interior. In later times, the anthropized space of the buffered cave was extended outwards with the construction of a structural module in barrel-vaulted masonry, called *lamione*.

The construction module is closed by a front façade with the characteristic scaled tympanum. The building heritage of Matera is a unique *monumentum* of the ancient building sustainability using local materials and construction scraps. The calcarenite materials of the horizontal and vertical closures come from the excavation of the hypogeum environments of buildings.

The blocks vary in size between 25-27 cm in height, 20-25 cm in width and 45-60 cm in length and are assembled with joints of mortar in masonry with thicknesses between 50 cm and 120 cm. The fine dust of scrap from the shaping of the blocks, called *tufina,* was recovered and reused as an inert component in the preparation of mortars. The mortar binder was an aerial or hydraulic lime obtained from the firing of calcarenites with varying degrees of clay minerals. Lime was also used for the whitewashing of the internal and external walls and for pigmented paints with the typical colours of pink, yellow and light blue.

Figure 2. Detail of a masonry with varying degrees of alveolization of contiguous ashlars.

Starting from the eighties of the last century, when a strategic plan for the recovery of the Sassi was launched, numerous restoration projects have been carried out. Various commercial products have been used to consolidate and protect the damaged surfaces of dug and built structures. The treatments of the surface in many cases were neither effective nor durable. Yellowing and detachments occurred over time due to the chemical, physical and mechanical incompatibility of acrylic and siloxane-based materials with the stone substrate. In addition, the repair and rebuilding of the mortar joints in the masonry with unsuitable materials and inadequate thicknesses have profoundly altered the aesthetic and formal value of the building surfaces.

The building heritage of the city of Matera gained popularity in 2019 when the city had the important recognition of European Capital of Culture. However, it is an extremely fragile heritage that requires continuous scheduled maintenance as it once did with the white washing of surfaces. The rocky surfaces of the hypogeum environments and the use of facing masonry in recent years also impose the requirement of transparency to the products for the preservation of surfaces. Organic or semi-organic polymers ensure the transparency of surfaces treatment. Unfortunately, these products dissolve easily in organic solvents that create health and safety issues for operators in the sector of restoration. There is therefore a need for product and process innovations that favor the use of environmentally friendly, non-toxic, and harmful for human health consolidating and protective materials. Finally, the microstructural variability of calcarenites prevents the use of simplified reasoning by typological analogy in the knowledge phase of the state of conservation of the property and requires analytical investigations for the characterization of the building materials and their forms of degradation.

3. The experimental campaign in the city of Matera

During the experimental activities carried out in cooperation with the Superintendence of Archaeology, Fine Arts and Landscape of Basilicata diagnostics was applied to the religious building heritage of the city of Matera. Diagnostic has been part of the research activities under the national project ‘Product and process innovation for planned and preventive maintenance, preservation and restoration of cultural heritage” funded by the Ministry of University and Research in the Smart Cities and Social Innovation program. Laboratory analytical techniques have been used for the characterization of calcarenites and their degradation forms. On-site diagnostic techniques have been used for the comparative evaluation of long-term effectiveness between innovative acrylic-urethane in aqueous solvent developed by industrial partner Icap Leather Chem SpAand commonly used consolidating and protective commercial products of building surfaces made of calcarenite. It is a friable limestone rock, widespread in the Mediterranean area, that is highly vulnerable to various forms of chemical, physical and biological degradation.

In the first phase of the research programme, the bibliographic research as well as discussion and sharing of experiences with the stakeholders of the restoration sector (owners and managers of the properties, restoration companies, producers of materials and technologies for restoration, restorers) have been carried out. The preliminary activities highlighted a great fragmentation of the technical-scientific literature. In addition, it was also found the absence in many cases of a multidisciplinary approach with the use of diagnostics in design practice.

The technical and safety data sheets of the commercial products most used for consolidation and/or protection of building surfaces in calcarenite have been evaluated. The consolidating products, applied both by spray and brush until saturation, contain ethyl silicate that in contact with water forms a silica gel filling the porosities with a cohesive effect even in substrates of a calcareous nature. The hydrophobic effect of the protectives is obtained using organic polymers based on silanes and siloxanes in an aqueous solvent applied by spray or brush.

Successively, an experimental design of intervention has been planned and developed in cooperation with the Superintendence Archaeology, Fine Arts and Landscape of Basilicata. Thanks to the adhesion to the experimental project of the Archdiocese of Matera, three churches have been chosen as case studies, each one in the three districts of the old city: San Pietro Barisano, with dug and built structures, in the north-western district of Sasso Barisano, San Francesco d'Assisi in the central district of Piano or Pianoro that once included the fortified city and Santa Lucia alle Malve in the south-eastern quarter of Sasso Caveoso.

The research activities carried out on the above-mentioned case studies can be summarized in the following phases: I) historical and archival investigations; II) acquisition of information on previous restorations; III) constructive survey with integrated top-down and bottom-up approaches for the identification of materials and technological elements; IV) pathological survey using the lexicon of the UNI 11182:2006 standard; V) design and execution of the diagnostic plan for microstructural characterization of calcarenites and their degradations; VI) verification of the effectiveness and cost assessment of cleaning, consolidation and protection treatments on sample areas of the case studies; VII) comparative verification of the medium and long-term effectiveness of innovative and commercial products for consolidation and protection of building surfaces through the use of non-invasive and easy-to-use diagnostic tools.

3.1. The diagnostic plan for microstructural characterization of calcarenites and their degradations

After the preliminary phases of acquisition of information on the construction and restoration history of the property and building and pathological survey, a diagnostic plan has been defined for the characterisation of calcarenites and their degradation in the three case studies of San Pietro Barisano, San Francesco di Assisi e Santa Lucia alle Malve. The diagnostic plan was approved by the Superintendence and was carried out in the presence of the supervisory staff of the protection agency. The experimental activities were carried out through the integrated use of the following laboratory techniques: 1) optical and electron scanning microscopy; 2) X-ray diffraction on powders; 3) micro-Raman spectroscopy; 4) X-ray microtomography. Light microscopy provides an initial description of the sample, giving morphological and textural information. Polarizing microscopy on thin sections allows the characterization of calcarenite according to Folk's classification (Folk, 1959). Scanning electron microscopy equipped with a microprobe

EDS (energy dispersive spectroscopy)gives morphological and structural information and enables semi-quantitative analysis of individual chemical elements. Diffractometric analysis allows the identification and semi-quantitative evaluation of the mineralogical phases. Micro-Raman analysis using a microscope connected to the spectrophotometer provides information on individual crystals or very small portions of the sample. X-ray microtomography allows the evaluation of the porosity of the sample.

A sampling campaign has been carried out with the collection of micro-samples in surfaces areas considered representative of the calcarenitic materials and their forms of degradation revealed by the morphological examination in the three case studies.

3.2. The case study of San Pietro Barisano

Sampling was carried out on the left (SP1, SP2, SP3) and right(SP4, SP5, SP6) sides of the façade of the church of San Pietro Barisano (Fig. 3). Microsamples were also taken on the right side of the apse for the characterization of the efflorescence widespread in all the interior surfaces of the church. Surface deposits and reddish, white and dark patinas are visible to the naked eye both on the left and right sides of the facade. Figure 4 shows the light microscopy images of the facade samples. Sample SP1is covered with abundant red and brown-black crystals. Small fractures containing yellow acicular crystals can also be recognised locally. Sample SP2 consists almost entirely of calcite crystals in which a few orange crystals are found. Sample SP3 is a fine powder taken in a degraded joint between two blocks. Sample SP4 appears as a smooth and compact white patina. Sample SP5 is a calcarenite with calcite crystals whose colour varies from white to yellow and rare brown crystals. Finally, sample SP6 consists of calcite crystals with dark surface parts.

Figure 3. Sampling of the façade of San Pietro Barisano.

Figure 4. Light microscopy images of the samples of the façade of San Pietro Barisano.

Samples SP1 and SP2 have been used for the preparation of thin sections observed with the polarizing microscope (Fig. 5). Sample SP1 is a biomicrite with secondary porosity not filled by cement or matrix. Sample SP2 is a bioclastic calcarenite with considerable unfilled primary porosity. X-ray diffractometry showed calcite and dolomite as the main mineralogical phases. Gypsum, nitratin, and akermanite were identified on the samples taken from the interior of the church.

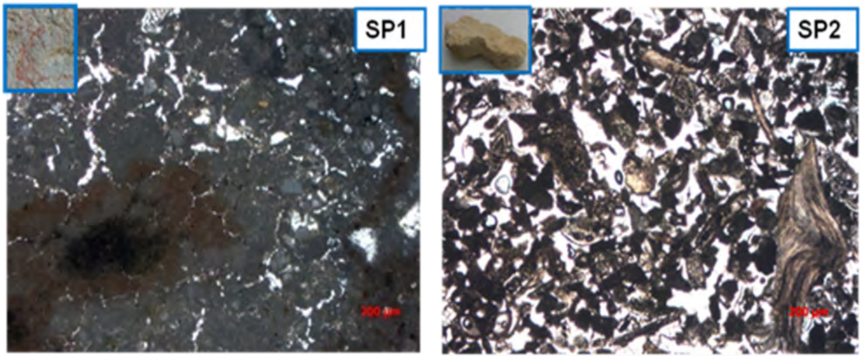


Figure 5. Polarizing microscopy images of sample SP1 (on the left)
and sample SP2 (on the right) of San Pietro Barisano.

Micro-Raman spectroscopy analysis was performed on all samples except for sample SP3, which was a fine powder. Red and brown crystals of the sample SP1 revealed the presence of haematite and magnetite, respectively. The white patina of sample SP3 is pure calcium carbonate, while the dark areas of the sample SP6 showed the calcite spectra. The dark part of the sample showed the spectra of C-C vibrations. X-ray microtomography investigations carried out on sample SP2 showed an open porosity of 42.7 %, a total porosity of 43.0 %, an average granule diameter of 73.5 μm and an average pore diameter of 72.9 μm.

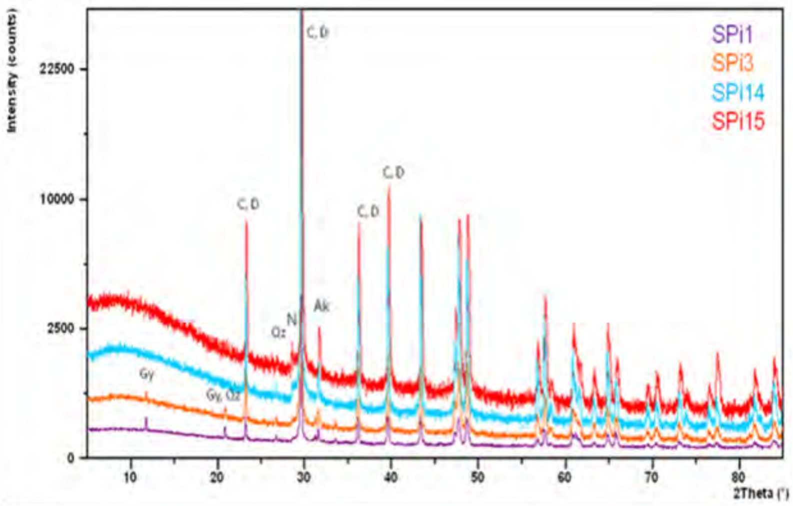


Figure 6. Diffractiongrams of samples taken from the interior of the Church of San Pietro Barisano. Caption: C = calcite $CaCO_3$; D = dolomite $MgCa(CO_3)_2$; Gy = gypsum ($CaSO_4$); Qz = Quartz, SiO_2; N = nitratin$NaNO_3$; Ak = akermanite, $Ca_2MgSi_2O_7$.

3.3. The case study of San Francesco d'Assisi

Sampling was carried out on the front and back façade of the church of San Francesco d'Assisi. Three samples were taken on the left-hand side of the front façade on the bottom areas seriously damaged by alveolization and blacking, while only one sample was taken on the right-hand side in a better state of conservation (Fig. 7). Six samples were taken from the back façade severely compromised by pulverization of ashlars and widespread white patina with reddish-black patinas (Fig. 8).

Figure 7. Sampling of the front façade of San Francesco d'Assisi.

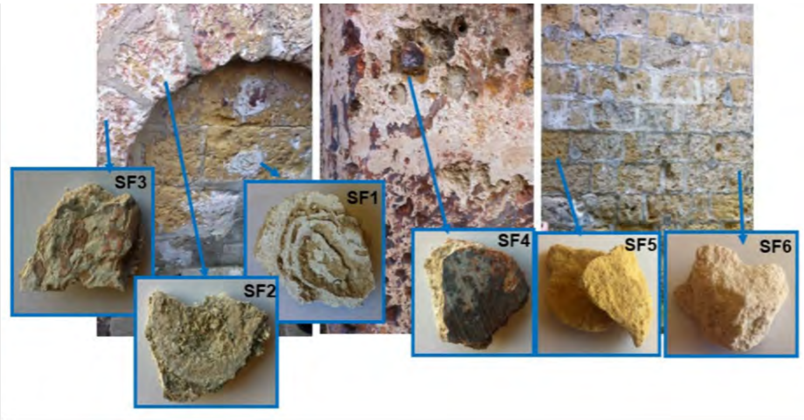


Figure 8. Sampling of the back façade of San Francesco d'Assisi.

Samples SF2, SF4, SF5 and SF6 of the back facade are biomicrites. All the samples of the front façade and samples SF4 and SF6 of the back facade are bioclastic calcarenites with secondary porosity (Fig. 9). XRD analysis showed calcite and dolomite as main mineralogical phases and quartz, iron oxides, halite (NaCl), gypsum, nitratin as minor component. SEM-EDS investigations performed on fragments of all samples showed the same phases detected with XRD and the presence of silicon, sulphur and iron in the patinas of the back facade. C-O stretching vibrations, calcium oxalates in the form of whewellite, $Ca(C_2O_4)\cdot 2H_2O$, gypsum and magnetite were identified by means micro-Raman spectroscopy.

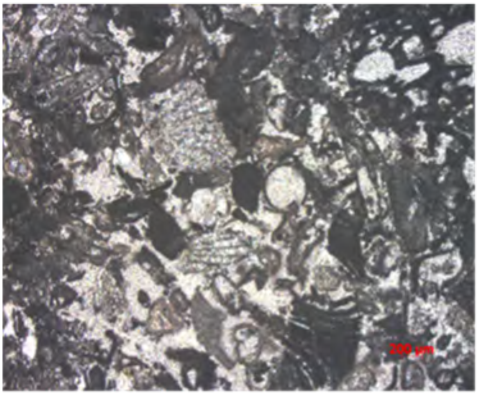


Figure 9. Polarizing microscopy images of sample SFFSX1 of the front facade of San Francesco d'Assisi.

3.4. The case study of Santa Lucia alle Malve

Sampling was carried out inside the church of Santa Lucia alle Malve, severely compromised by the widespread presence of biological colonisation due to water infiltration. Four samples (SL1, SL2, SL3, SL4) were taken in the rock walls in the lower parts without frescos (Fig. 10). Figure 11 shows the light microscopy images of four samples. The thin sections of the four samples were observed under a polarising microscope for petrographic analysis.

SL1is a biomicrite with silica clasts characterised by secondary unfilled porosity. This sample also shows a patina of alteration in which the original material is hardly recognisable. Sample SL2is a bioclastic calcarenite with the presence of intraclasts and unfilled primary porosity. Sample SL3 is a bioclastic calcarenite with considerable unfilled primary porosity. Patinas and silicoclastic materials are also present. Sample SL4 is a calcarenite with unfilled primary porosity and many intraclasts. XRD analysis showed that all samples contain calcite as the predominant phase and quartz as the minor phase. In addition to these phases, there is only gypsum in sample SL3 and gypsum and halite in sample SL1. A modest amount of kaolinite is also found in the pattern of sample SL2. Raman investigations revealed the presence of calcite crystals, calcium oxalate dihydrate and carboxyl groups on the surface of the analysed samples X-ray microtomography investigations carried out on sample SL2 showed an open porosity of 36.5, a total porosity of 36.6 %, an average grain diameter of 84.3 µm and an average pore diameter of 59.9 µm.

SEM observations of the samples showed the presence of lithoclasts and fossils. At higher magnifications, the presence of both calcite crystals partially covered by a very fine silica component and organic substances with a root-like and/or spherule-like appearance can be detected on the surface of the rock fragment.

Figure 10. Sampling in the interior rock faces of the church of Santa Lucia alle Malve.

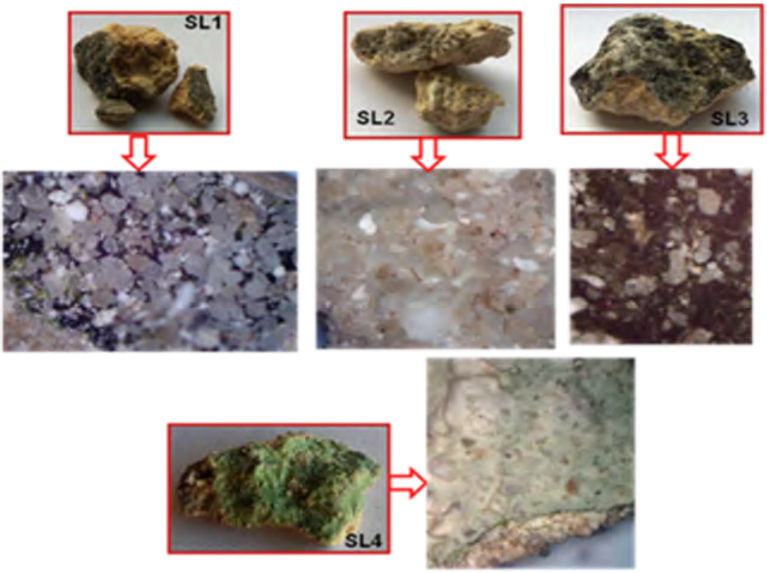


Figure 11. Light microscopy images of the samples of the interior rock faces of Santa Lucia alle Malve.

4. Experimental intervention of cleaning, consolidation, and protection of building heritage surfaces

After the execution of the diagnostic plan, intervention of cleaning, consolidation and protection were planned and carried out in sample areas of the following case study: the interior and exterior surfaces of the church of San Pietro Barisano; the exterior surfaces in calcarenite rock and masonry of the bell tower of the church of San Pietro Barisano; the lower left side of the front façade of the Church of San Francesco d'Assisi; the interior and exterior surfaces of the church of the Madonna dei Derelitti in the Park of Rupestrian Church. The latter church was chosen as an ongoing case study, due to the closure of the church of Santa Lucia alle Malve for restoration work.

The activities were carried out in collaboration with restoration companies under the supervision of the Superintendency's restorers. During the experimental interventions, data on the consumption of materials, labor and equipment hire per square meter of treated surface have been noted for the verification and implementation of new reference price lists included in the digital platform for heritage maintenance of the project.

Both chemical, manual and mechanical treatments were tried out for cleaning. A pre-mixed commercial mortar based on lime and pozzolan was used to fill the degraded joints of a masonry sample area of the bell tower of the church of San Pietro Barisano (Fig. 12). An experimental mortar prepared in situ with aerial lime and an innovative acrylic-urethane product in aqueous solvent developed by the industrial partner Icap Leather Chem SpA was used for filling a cavity of a sample ashlar on the left side of the facade of San Francesco d'Assisi (Fig. 13).

Both commercial products and new pilot acrylic-urethane products in an aqueous solvent produced by the industrial partner Icap Leather Chem SpA were used for the consolidation and protection of the rock and masonry sample area.

Four commercial products have been tested: 1) an ethyl ester-based consolidating product; 2) a protective containing silanes and siloxanes; 3) a consolidating and protective product based on ethyl ester and silanes and siloxanes; 4) a self-cleaning product containing titanium dioxide nanoparticles.

Three new acrylic-urethan products labelled as POLYRESTP2, AC012, HR2 were solved in distilled water and applied on sample areas with dilution ratios of 1:4, 1:6, 1:8, 1:10, 1:12 and 1:14 (Fig. 14).

Spray and brush application tests were carried out for all products until saturation of sample surfaces. Environmental conditions (temperature and humidity) were noted during the treatment as well as the judgement of the operator on the products' behaviour (ease of application, tendency to foam, ease of absorption etc.) were recorded.

Figure 12. Remaking of the degraded joints in the sample area of the masonry of the bell tower of San Pietro Barisano with a pre-mixed commercial mortar based on lime and pozzolan.

Figure 13. Filling of the alveolized cavity of the sample ashlar on the left side of the facade of San Francesco d'Assisi with an experimental mortar containing aerial lime and an acrylic-urethan product in aqueous solvent developed by the industrial partner Icap Leather ChemSpA.

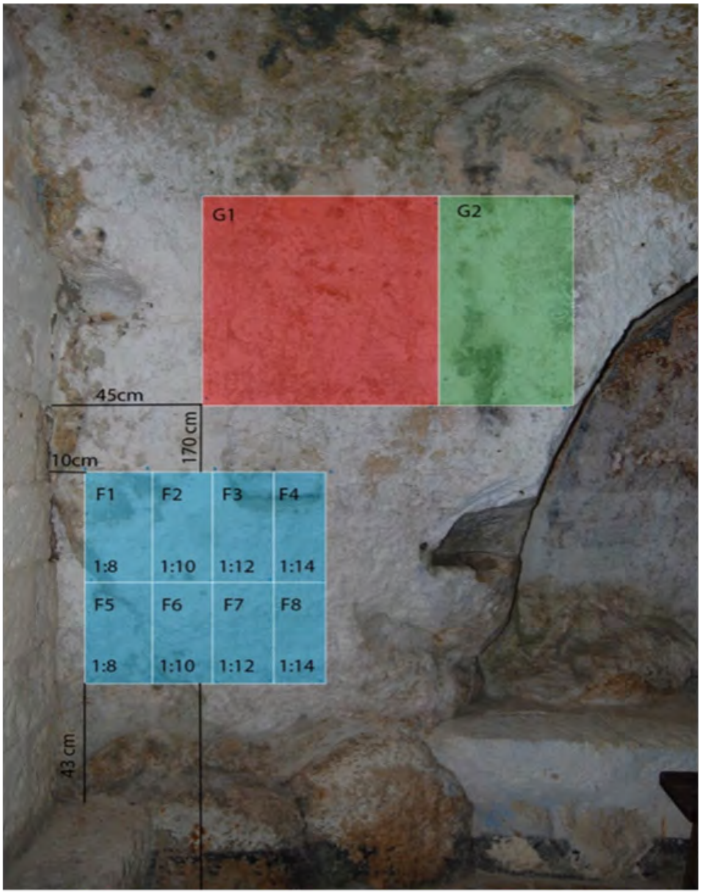


Figure 14. Treatments of sample area in the interior surfaces of the church of Madonna dei Derelitti with the pilot products POLYRESTP2(F1-F4) andAC012 (F5-F8) and commercial ethyl silicate products (G1-G2).

Non-invasive and cost-effective diagnostics were defined to verify the medium and long-term effectiveness of both the pilot products developed by the industrial partner and the commercial consolidating and protective products. It consists of the colorimetric test, scotch tape test and water absorption (Fig. 15).

Colorimetric test determines the chromatic variations induced by treatments (UNI EN 15886:2010). The instrument used is a Konica Minolta CM-2600d spectrophotometer. The chromatic values are expressed according to the L*a*b*colour space of CIE (Commission Internationale d'Eclairage), where L* is the brightness coordinate, a* (red/green) and b* (yellow/blue) are the coordinates that define the hue (positive values of a* fall in the red zone, negative values in the green zone; positive values of b* fall in the yellow zone, negative values in the blue zone). Measurements were carried out using an aperture with a diameter of 8 mm, specular component excluded (SCE), illumining D65 and viewing angle of 10°. The results obtained represent the average of 3 measurements taken on the untreated area and on each area treated with different products.

Figure 15. Non-invasive and cost-effective diagnostics to evaluate products behaviour. Colorimetric Test on the left; Scotch Tape Test in the middle; Water Absorption on the right.

The scotch tape test, called also the peeling test, is used to assess the degree of cohesion of a stone surface (ASTM D3359-08, 2008). A strip of adhesive paper with known dimensions (50 x 22 mm) is weighed with an analytical balance with a sensitivity of 0.1 mg; it is then pressed onto the stone surface and left to adhere to it for 90 seconds. The difference between the initial weight and the final weight of the strip corresponds to the weight of the stone material detached from the support; this quantity reflects the cohesion characteristics of the stone. The test was repeated four times at each point.

The water absorption test uses the contact sponge method to assess the degree of water repellence and reduction of porosity determined by products applied to stone surfaces (UNI 11432:2011). The measurements were carried out on treated and untreated areas, using a quantity of water equal to 5 ml and a contact time of 1 minute.

The pilot product developed by the industrial partner Icap Leather Chem at lower dilution ratios showed chromatic variations slightly higher than the threshold $\Delta E=5$ perceivable to the naked eye. The best behavior in terms of colorimetric variation was obtained with the product POLYRESTP2 with a dilution ratio of 1:14.

The product HR2 with a dilution ratio of 1:4 and the self-cleaning commercial product showed the best hydrophilization of surfaces.

The greatest degree of cohesion of the calcarenite substrate was obtained in the sample area treated with the pilot product HR2 with a dilution ratio of 1:4.

5. Conclusions

The work highlights the key role of diagnostics in all phases of the conservation process of building heritage. Diagnostics indeed, supported by a sound knowledge of building materials and technologies, allows the assessment of the state of conservation of the asset and the choice of sustainable interventions that to meet both the criteria of compatibility, reversibility and recognisability and the criteria of economy, minimal impact on the environment and human health.

Diagnostics is also a strategic tool for the prevention of degradation phenomena and for the evaluation of the effectiveness and durability of interventions.

The use of non-invasive investigation techniques together with the adoption of sustainable materials and technologies is a fundamental means of preserving the integrity of the artifact and the identity value of the asset, with its dual value of aesthetics and historical testimony.

Acknowledgements

The research activity is part of the project 'Product and process innovation for planned and preventive maintenance, preservation, and restoration of cultural heritage' funded by the Ministry of University and Research under the Smart Cities and Social Innovation program.

References

ASTM D3359-08: 2008, *Standard Test Methods for Measuring Adhesion by Tape Test*, ASTM International, West Conshohocken, PA.

G.F. Andriani - N. Walsh, *Physical properties and textural parameters of calcarenitic rocks: qualitative and quantitative evaluations*, «Engineering Geology», 67(1-2), (2002), pp. 5-15.

G. Bernardo, - A. Guida, *Heritages of stone: materials degradation and restoration works,* Proceedings of 3th International Conference on Documentation, Conservation and Restoration of the Architectural Heritage and Landscape protection (22-26 October, Universitad Politecnica de Valencia), ReUSO 2015, Valencia 2015, pp. 299-306.

R.L. Folk, *Practical petrographic classification of limestones*, «American Association of Petroleum Geologists Bulletin», 43 (1959), pp. 1-38.

P. Pieri - L. Sabato - M. Tropeano, *Significato geodinamico dei caratteri deposizionali e strutturali della fossa Bradanica nel Pleistocene,* «Mem. Soc. Geol. It », 51 (1996), pp. 501-515, 7ff.

M. Tropeano - M. Schiattarella, *Un parco geologico urbano per i Sassi di Matera,* in *SASSI DI MATERA Per una nuova stagione,* a cura di A. Colonna, M. Morelli, A. Percoco, V. Santochirico, Milano, Collana Percorsi, 1/2019, pp. 160-169.

UNI 11182 Beni culturali: 2006, *Materiali lapidei naturali ed artificiali: descrizione della forma di alterazione - Termini e definizioni / Ente Nazionale Italiano di Unificazione.*

UNI 11432: 2011, *Beni culturali - Materiali lapidei naturali ed artificiali - Misura della capacità di assorbimento di acqua mediante spugna di contatto.*

UNI EN 15886: 2010, *Conservazione dei Beni Culturali - Metodi di prova - Misura del colore delle superfici.*

Carmine Schiavone
Tab Consulting s.r.l., Potenza
Domenico Filitti
Exo - Organismo di ricerca Società Consortile a r. l., Potenza

The HeMain Technology Platform

ABSTRACT

«HeMaIn» is a process innovation that, along with research and development of innovative products, aims to carry out actions to manage available resources and cultural policies by creating a technological platform scheduling preventive maintenance interventions. The synergistic and multidisciplinary actions resulted from ICT technologies, and chemical, architectural, and biotechnological knowledge. The technology platform deals with:

- cataloging the Asset taken in charge;
- studying its morphology and measuring its geometries;
- retrieving equipment, in situ and ex-situ measurements, and data, from a sensor network;
- managing a catalog in which information regarding the Asset is stored and classified together with the “records” of interventions;
- managing a system of “data storage” and processing, a predictive model for the economic evaluation of interventions, a “governance” software based on a metadata system;
- supporting programming activities of maintenance interventions based on macro-indicators.

KEYWORDS

HeMain, Cultural Heritage, Preventive maintenance, Intervention planning, Decision Support

RIASSUNTO

«HeMaIn» è un’innovazione di processo che, oltre alle attività di ricerca e sviluppo di prodotti innovativi, attraverso l’azione sinergica e multidisciplinare di competenze derivanti dalle tecnologie ICT e dalle tecnologie chimiche, architettoniche e biotecnologiche, si è proposta di realizzare azioni e interventi per la gestione delle risorse disponibili e per le politiche culturali mediante lo sviluppo di una piattaforma tecnologica di programmazione degli interventi preventivi di manutenzione. La piattaforma tecnologica si occupa di:

- catalogare il Bene preso in carico;
- studiarne la morfologia e misurarne le geometrie;
- recuperare dati da una rete di sensori e da misure di strumentazioni in situ ed ex situ;
- gestire un catalogo in cui vengono conservate e classificate le informazioni del Bene e il “registro” degli interventi;

- gestire un sistema di “data storage” ed elaborazione, un modello predittivo per la valutazione economica degli interventi, un software di “governance” basato su un sistema di metadati;
- supportare le attività di programmazione degli interventi manutentivi sulla base di macroindicatori.

PAROLE CHIAVE

HeMain; Beni culturali; Manutenzione preventiva; Programmazione interventi; Supporto decisioni

Introduction

The preservation of cultural heritage requires the development of increasingly innovative, effective, long-lasting, and less expensive protection strategies. Despite the Legislative Decree 22 January 2004, n. 29 provides for the ordinary planning of cultural heritage, the current restoration and conservation interventions have a curative and not preventive actions. These are available only in case of a huge loss of historical material or huge damages.

Furthermore, hitherto, no policy for implementing maintenance management of cultural heritage makes widespread use of ICT (Information and Communication Technologies) technological solutions. In this context, “HeMaIn” (Product and process innovation for Sustainable and Planned Maintenance, Conservation, and Restoration of Cultural Heritage), an Industrial Research and Experimental Development Project (Ministry of Education Smart Cities And Communities And Social Innovation | Research Project SCN_00520) was developed. Several academic and industrial partnerships worked on the project: “Ca’ Foscari” University of Venice, “Sapienza” University of Rome, University of Basilicata, University of L’ Aquila, Tab Consulting S.r.l., ICAP Leather Chem S. p. a.

It is a process innovation that, along with research and development of innovative products, aims to carry out actions to manage available resources and cultural policies by creating a technological platform scheduling preventive maintenance interventions. The synergistic and multidisciplinary actions resulted from ICT technologies, and chemical, architectural, and biotechnological knowledge. The platform’s main features are briefly described in the following paragraph.

The technological platform for planning preventive maintenance interventions

Each heritage structure has its own features due to several changing factors. There are building techniques, materials, age, history, building context, and functional destination to consider (it is wider and more problematic in case the real estate constitutes or preserves cultural heritage). A decision support and analysis system, or the technological platform for planning preventive maintenance interventions, inevitably carries out its action starting from the direct assessment of the Monument or, more generally, of the Asset taken in charge.

For this reason, a preparatory and essential step is a good knowledge of the Asset to monitor. It can be achieved by employing all available non-invasive or minimally invasive tools and techniques. The first step in taking charge of an Asset is classifying it. It has been developed a cataloging model in compliance with the system defined by the Central Institute for Catalog and Documentation (ICCD). The model was implemented in the Technology Platform and integrated with a decomposition and classification system coming from previous well-known and used systems.

Asset evaluation first and cataloging later, enable to identify, highlight and analyse the multiple features of the object (shape, structure, individual elements, composition, relationships between parts and the whole, the material and chromatic features, the state of conservation and any critical situations, historical evidence, temporal and spatial evolution). Hence the need to reach a detailed knowledge of the objects through high-quality surveys, not aimed to represent an estimated and conjectural generic shape, but aimed to provide its actual and objective shape. The technological platform is equipped with a special module for the visualization and management of point clouds, in addition to having systems for the georeferenced representation on the map of the considered real estate and for displaying photos (any sort, even spherical) from georeferenced observation points and represented in Google Maps environment. It also provides specific data storage of the Asset or portions thereof. This solution allows the association with each constituent element of the Asset, images, thematic plants, thermographs, text documents, and files of multiple kinds.

The Technological Platform provides modules for the acquisition, organization, and processing of heterogeneous data through networks of sensors for monitoring the most representative parameters of the state of conservation of the cultural heritage (and to derive, from these, useful indicators of environmental conditions of conservation, such as those described in UNI 10829 (1999).

The advanced technologies and techniques available today allow the efficient detection of reliable indicators related to the state of specific structures, allowing to study (quickly and at affordable costs) local and/or global aspects related to their state of conservation and safety, drastically reducing time and number of inspections by technicians and allowing at the same time, the collection and sharing of data, information, and significantly larger images, in quantity and reliability, compared to ordinary methods of detection. One of the main tasks of the Technological Platform is to make them easily accessible, usable, consultable, manageable, and shareable. The main characteristics can be summarized in the following list:

- multi-tier service-based architecture, cloud-ready;
- persistence layer based on optimized and diversified storage systems: Database Document Oriented and Object Oriented;
- use of open free products and technologies;
- adherence to national and international industry standards;
- integration of features for the management, cataloging and visualization of images and 2D/3D data acquired through laser scans, thermographs, etc;

- it enables the classification of architectural cultural heritage in all their components, including objects considered as works of art, structural, architectural, plant engineering, technological elements, etc., Furthermore, it allows to store and manage a set of structured and non-structured information in formats and using tools for effective and easy consultation (documents, photographs, videos, 3D models, videos, graphs, etc.);
- it integrates a module for the acquisition of near real-time data from sensor networks or measuring instruments through the main communication protocols (serial, Modbus, HTTP, ZigBee);
- it enables the configuration of complex indicators for the monitoring of acquired parameters and the notification of alert situations to authorized operators;
- it integrates the implementation of a predictive model for the economic evaluation of maintenance interventions developed by "Sapienza" University of Rome;
- it enables the planning, management, and monitoring of ordinary and extraordinary maintenance activities, making it possible to monitor the progress and notify anomalous situations (delays, overruns of expected costs, changes in the way interventions are performed);
- it integrates a dashboard of analysis and decision support for decision-makers and professionals that enables easy access to information of technical, economic, chronological, and administrative interest along with the possibility of using a predictive model for the economic evaluation of maintenance interventions and a tool used in evaluating intervention costs (based on a price list elaborated within the Project).

Cataloging model

Cataloging cultural heritage is the essential cognitive tool for the correct and effective performance of the functions allowing the pursuit of protection and conservation objectives. At the same time, it constitutes an essential support for the management and enhancement of heritage, immovable and mobile; it is also vital in promoting and implementing educational, popular, and research activities.

Cataloging represents the moment of recognition of the Asset in its physical essence and its historical value (past and present). It consists in identifying, documenting the Asset, and properly storing the information collected according to precise criteria.

As part of the Project, it was developed and used a cataloging model with the system defined by the Central Institute for Catalogue and Documentation (ICCD), integrated with a decomposition and classification system derived from other widely known and used systems. The model works by melting together morphological decomposition criteria, a technological approach derived from UNI 8290:1(1981), and the relationships system between objects adopted by the ICCD standard. Compared to other cataloging solutions already in use, the model also combines additional and functional information in order to adapt the classification to the logic and functionality of the Technological Platform.

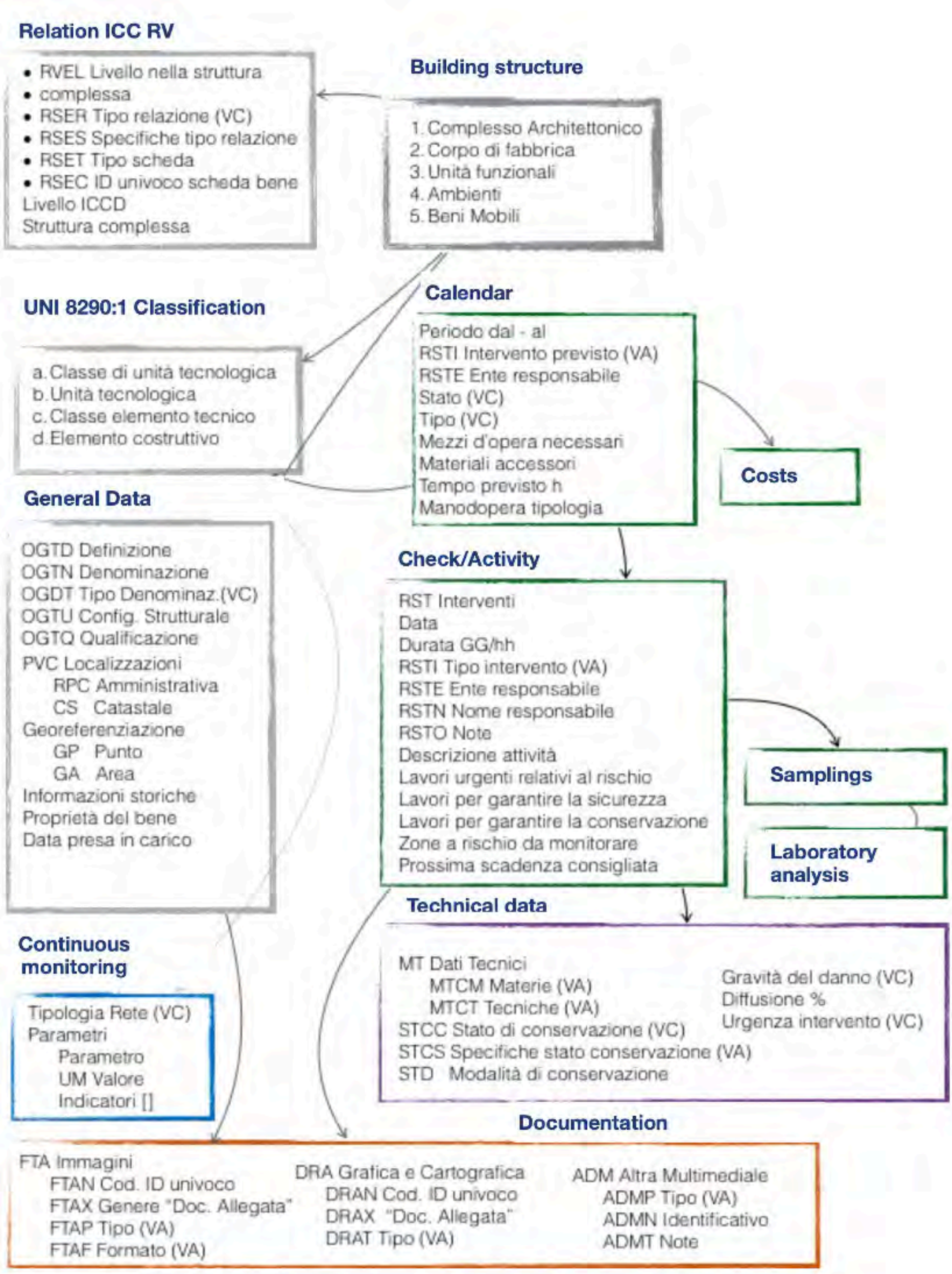


Figure 1. The main entities of the platform and their relationship.

The choice to refer to mature classification systems and rules shared at a national level allows the exchange of information between the different subjects (public and private) operating in the field of cultural heritage. It facilitates the establishment of the national heritage catalog provided by the Code of Cultural Heritage and Landscape. (D. Lgs.42/2004 and subsequent amendments, Art. 17).

In particular, the architectural Asset is broken down into control volumes within which the "Elements" are contained, that is, the objects on which it is possible to carry out inspections and/or maintenance.

The "Architectural Complex "is the volume that contains all the architectural Assets and is composed of additional smaller control volumes, defined as" Buildings "and" Environments "(the latter type represents the lower level control volume, which can be contained in" Buildings "and in the" Architectural complex").

The scheme in Figure 1 reports the main classes of entities managed within the platform, the most important attributes, and the relationships that bind those entities to each other. As can be seen, many of the attributes refer to the ICCD encoding and it is indicated whether the allowed values belong to a Closed (VC) or open (VA) Vocabulary.

The following macro-groups of Entities are identified: 1) identification, decomposition, description, and classification of the Asset; 2) data from continuous monitoring networks; 3) technical data (materials, techniques, state of conservation, risk); 4) documentation (images, cartographic, graphic, other multimedia); 5) planning and verification execution, inspections, maintenance, and sampling.

Each "Element", like each control volume, is classified according to the above classification model described.

The Technological Platform also allows storage and management of a database consisting of the accompanying documentation (documents, images, surveys, etc.) of each "control volume ("Architectural complex", "Factory Building" and "Environment"). In addition, it refers to each element in these contents, to carry out the monitoring activities and hence planned management.

Management of geometric data (position, shape, size)

To face the problem of preventive maintenance of cultural heritage, from a necessary synergistic and multidisciplinary skills approach, the need arises to reach the detailed knowledge of the objects preparatory to other activities (i.e. restoration) through high-quality surveys.

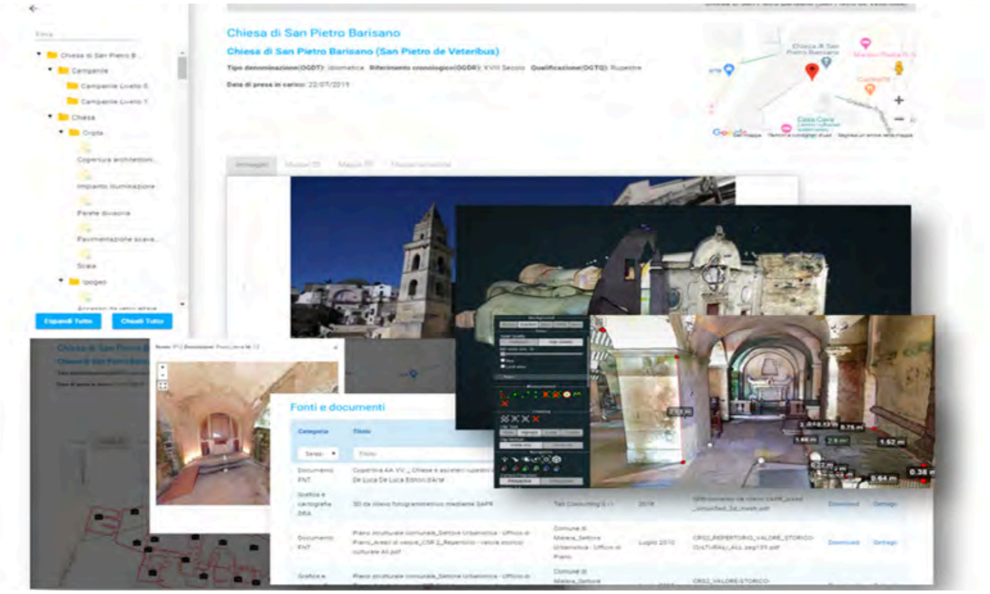
Surveys should not be oriented to the representation of a generic, approximate, and conjectural shape, but should provide details on the actual and objective shape, with all its irregularities, which might be more or less severe, and aesthetic, technical, or historically interesting (Foramitti, 1972).

The only advantage in addition to the traditional projections on main reference planes is also a three-dimensional representation of the data, which is in itself an added value.

The latter is, in fact, the most immediate and truthful representation, and makes possible a series of further insights, such as, for example, the analysis of collapse dynamics, the monitoring over time of variations, the virtual visualization of restoration interventions, etc.

There is a wide variety of techniques for making a three-dimensional relief. These techniques can be distinguished according to the size scale of the object they can detect, and the number of acquisitions. The detection techniques with the new high-resolution technologies introduce the great advantage of postponing the interpretative-subjective phase to the acquisition one. The possibility of preliminarily acquiring, in time and at reasonable costs, an enormous amount of data and subsequently being able to manage, filter and compare them effectively, opens the prospect of greater objectivity of the evaluations and a continuous extension of the analysis in compliance with an increasing multidisciplinarity that can study and deepen different themes.

Scanning measuring instruments that use laser sources, make it possible to acquire object shape information through a mathematical description (the "point cloud" or the mesh surfaces) that returns images of it from arbitrary points of view and under arbitrary light conditions (Blais, 2004). In particular, the short-range terrestrial laser scanner is a high-resolution three-dimensional detection technology, which allows to obtain huge amounts of data through non-contact methods. This non-contact method is particularly useful in the field of surveys on cultural heritage, as it is essential to minimize the invasiveness of any diagnostic and study technique. In the interpretative phase, appropriate post-processing allows measuring, highlighting, and monitoring aspects that are complicated to observe or quantify (such as deformations or the evolution of cracks), guaranteeing the exploration without necessarily going on-site or minimizing in situ reconnaissance.



Chiesa di San Pietro Barisano

Chiesa di San Pietro Barisano (San Pietro de Veteribus)

Tipo denominazione(OGDT): Idiomatica Riferimento cronologico(OGDR): XVIII Secolo Qualificazione(OGTQ): Rupestre

Data di presa in carico: 22/07/2019

Figure 2. Some screenshots of the technological platform interface highlighting the case study (Church of San Pietro Barisano) in Matera.

Figure 2 shows some screens of the interface of the technological platform in which they highlight: the main screen of a case study (Church of San Pietro Barisano in Matera) with the sidebar (which shows, according to a tree representation, the "architectural complex" with its "buildings", the "environments" and the "elements"), the point cloud of the architectural complex, the georeferenced plan on the map of "Google Maps" with spherical photo shooting points and the pop-up photo display, a table of document storage table accompanying a control volume.

The Technology Platform is equipped with a cataloging and visualization laser scans 3D web software, the "Point Cloud Viewer". The system is integrated into the consultation sheet of the assets that are part of the catalog developed in the Project and provides the following characteristics:

- possibility of loading 3D scans for via web distribution;
- ability to manage supported formats;
- possibility to pre-process 3D data in the formats provided for subsequent distribution via HTTP;
- possibility to view the data, uploaded to the browser, that support WebGL through a specific display.

The Point Cloud Viewer enables the creation of a repository of pre-processed 3D scans parallel to the actual data catalog to enable their subsequent visualization via a web application. An additional feature provided by the viewer, and implemented in the platform, allows the definition of a specific area of the 3D scan through a clipping functionality. In this modality, a viewpoint and section of the data can be established for later viewing. This functionality does not create new data but always accesses the same original data by showing only a portion (typically a "control volume such as the "Architectural complex", a "Factory Body", an "Environment" or each element (therein contained) which, at the discretion of the user, can also be further resized.

Associated with the Property in question, it is also possible to insert images (for each of which a special cataloging card can be filled in) and represent the shooting points within a kml plan (in this way the elaboration can be implemented in the software and represented in its context through a GIS, Google Maps or Google Earth; the user interface of the technology platform, shows these files in specific sections depending on Google Maps). As a result, it not only ensures a picture and georeferencing of the shooting point but also its immediate identification on the planimetry. This tool allows the user to navigate the Asset in an effective and nimble way, whilst lacking performance hardware (e.g., mobile devices such as mobiles or tablets).

Systemating Monitoring

The Technology Platform integrates modules for the acquisition, management, processing, and graphical representation of heterogeneous data deriving from networks and monitoring activities. In particular, in addition to the microclimate indicators, the Platform, in its current configuration, allows the acquisition of data related to indoor and outdoor measurements, as well as implementing and processing data useful for the management of maintenance activities (inspections and interventions).

Through the "Dashboard" control it is possible to view (on a quick reading digital" dashboard") the status of maintenance activities and some instrumental monitoring parameters of each of the Assets taken in charge. Appropriate symbols indicate the presence of critical conditions or those that need attention. The platform can also be integrated with additional modules for monitoring indicators (also in near-real time) such as those aimed at verifying the behavior of the structure.

The microclimate monitoring network

As it is well known, the role of the microclimate in the mechanisms of genesis and evolution of material degradation phenomena is decisive and, therefore, the study of the microclimatic characteristics (induced by natural and/or artificial environmental factors) of the architectural envelopes constituting and/or containing cultural heritage constitutes a useful tool for the analysis and management of a predictive maintenance model to support those involved in the prevention, preservation, and restoration of works.

Microclimatic monitoring is, in fact, one of the main tools for the evaluation and diagnosis of the aforementioned phenomena and, consequently, for the knowledge and conservation of Cultural Heritage. Specifically, it comes from a technical-cognitive development matured in different scientific areas attributable above all to the natural sciences, atmospheric physics, and meteorology (Camuffo, 2014).

For proper assets conservation in the museum and especially in the architectural field, it is necessary to monitor (and possibly modify) climatic parameters such as temperature, humidity, solar radiation, lighting, and the presence of pollutants. Furthermore, it is necessary to identify risky situations and establish thresholds of attention and alarm below which the conditions for conservation are optimal and, therefore, would allow procrastination of certain maintenance interventions or, conversely, above these limits, conditions are such to result in the acceleration of the normal degradation processes of the materials and consequently require more frequent routine maintenance interventions or in situ deepening and probably extraordinary maintenance interventions.

The complexity and variety of the objects that constitute the cultural heritage make it particularly difficult to identify and clearly define ranges and limits of environmental parameters, considered critical and optimal values, for the good preservation of the works. Therefore the correct use of reference tables must always be accompanied by a specific interpretation methodology based on the following points:

- evaluation of the state of preservation of the artifact;
- study of the trends of microclimatic parameters, lighting, and air quality of the environment in which the artifact is located (Figure 3). Cognitive element of considerable importance is the so-called "historical climate" which, if not known, should be mea-

sured at least for a year or whole multiples of it (UNI EN 15757, 2010). It is the microclimatic condition in which an artifact has been previously maintained. In these conditions artifact and climate were naturally compatible; otherwise, the artifact had to acclimatize risking irreversible dimensional deformations including the formation of cracks that basically have the function of creating the degree of freedom necessary to release the accumulation of internal stress and allow the material to respond to the seasonal/daily variability of climatic forces;
- overall assessment "state of conservation/environment";
- knowledge of the interaction between the artifact and the environment.

The concepts mentioned so far are for the most part information known since the last century. However, only today technological advances allow the creation of sensor systems, data collection, and data processing systems at the same costs, of installation, and management, such that they can be installed on a large number of assets, thus allowing to optimize the maintenance programs and interventions on a larger portion of the Cultural Heritage.

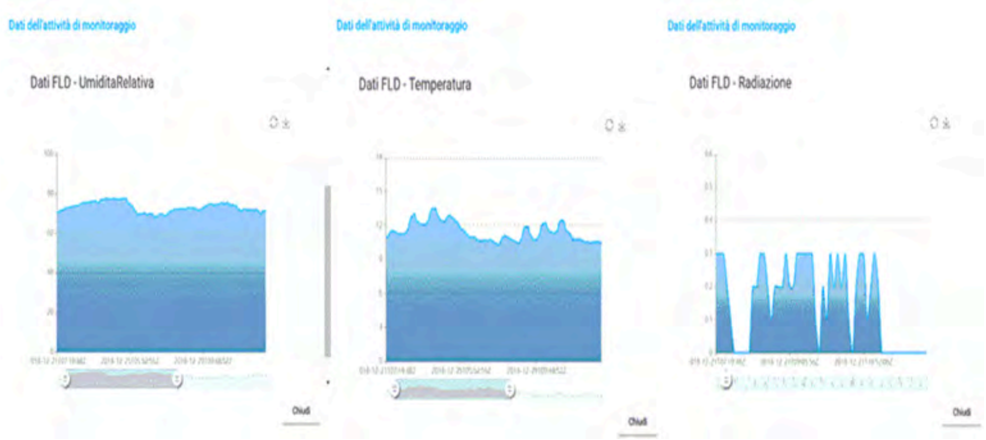


Figure 3. A screen of the microclimatic parameter monitoring module.

As part of the aforementioned Project, we also designed and prototyped a wireless network of data acquisition devices (WSN) that can be interfaced with a wide family of low-cost sensors and measuring equipment, primarily with all the sensors selected among those able to measure the most representative parameters of the state of conservation of the Asset and the possible causes of probable induction to the degradation of the Asset itself. Both low-level interfacing and data transmission issues with low-power protocols were addressed and solved by developing and testing appropriate firmware for the low-power microcontrollers that were used. In order to have the greatest elasticity of installation and low impact on the Asset to be monitored among the prerequisites imposed in the design phase, in addition to cost and low power consumption, were taken into account: the size and weight of the devices; the configurable network topology (mesh, so as to distribute computing resources and packet dissemination responsibilities over multiple nodes); the possibility of local data storage for later deferred transmission for contexts lacking a suitable Internet connection capable of real time conversations with the Platform; security aspects; and the possibility of using "local intelligence" to trigger alarms and control logic operating apart from the Platform.

The Platform, in addition to acquiring and displaying the data detected by the sensors, allows the calculation of derived parameters such as "deviation indicators" (UNI-EN 10829, 1999), and represents them in the pages dedicated to the monitoring of microclimatic parameters (Figure 4).

The data that can be acquired also allow in accordance with UNI-EN 15757 (2010), monitoring of temperature and relative humidity to preserve cultural heritage by limiting physical damage caused by tension-deformation cycles in objects containing hygroscopic organic materials. This category of objects includes wooden elements and structural components such as floors, doors, cladding and lintels, paintings, books, graphic documents, textiles, and objects made of bone, ivory, or leather.

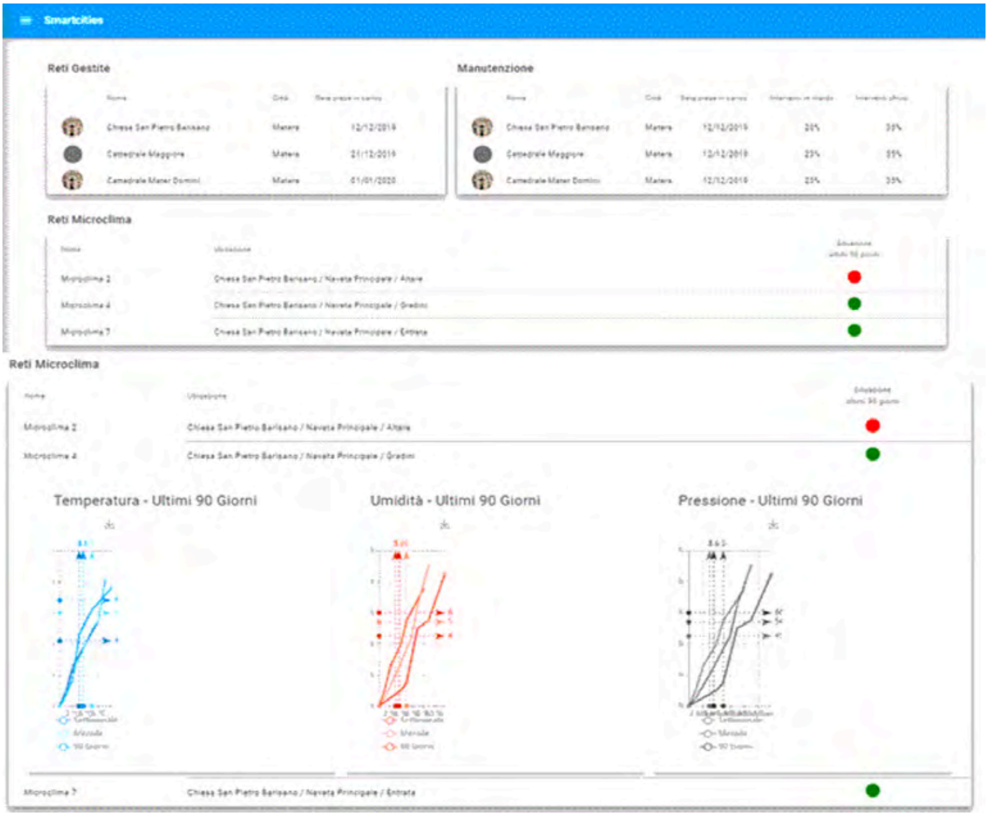


Figure 4. Control dashboard of microclimatic parameters and graphs of some related summary indicators.

The Platform enables to view an account of measurements and processing, which therefore includes:

- sufficient information to identify the space in which the surveys were carried out, the techniques and instruments used, the periods of carrying out the surveys, the operators, and the processing procedures adopted;
- the reference values adopted for the calculation of the deviation indicators referred to in the previous point, and the criteria used to define those reference values, in relation to the objects or categories of objects placed in the examined space;
- the values of the deviation indicators mentioned in the previous point, and the reason why some of them are omitted (e.g. because they are considered insignificant, because the relative measured values are not available, etc.);
- the average, maximum, and minimum values of temperature and humidity as well as the maximum values of their excursions on a daily basis, on a monthly basis, or on differen time intervals deemed significant.

With reference to UNI-EN 16242 (2013) other relative humidity-related quantities can be derived from three basic parameters: temperature, relative humidity, and atmospheric pressure. From the point of view of monitoring Cultural Heritage among the most useful are:

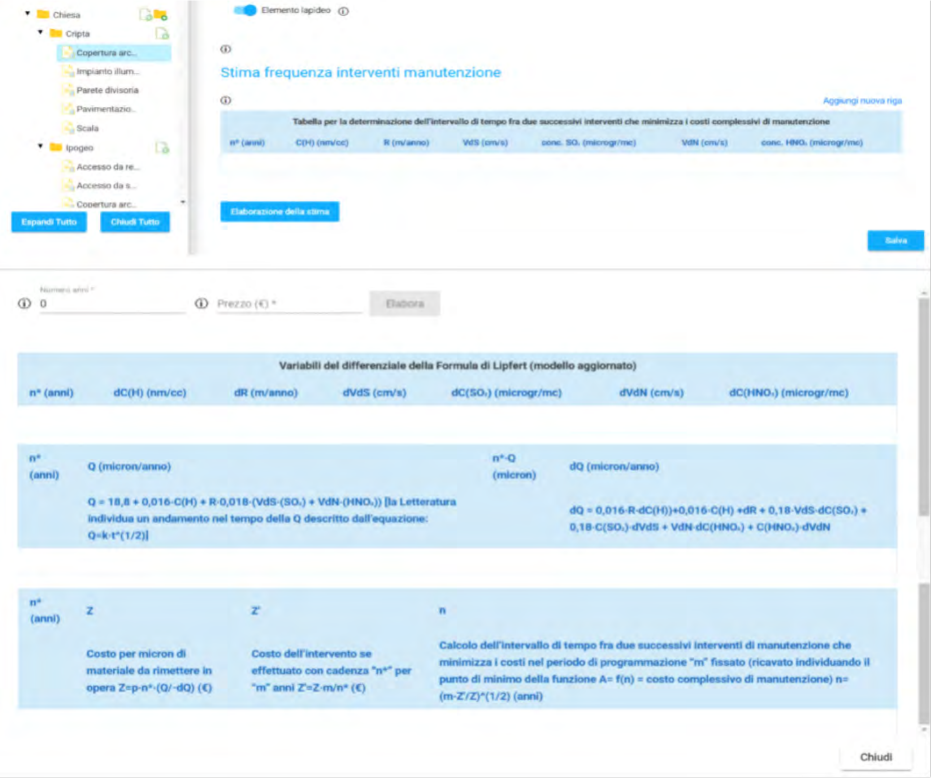
- Absolute humidity;
- Dew temperature;
- Mixing ratio.

Monitoring interventions

The “Task Plan Management” section enables to plan, implement and monitor the execution of maintenance activities on each of the components of the Assets taken in charge. This tool enables to store and share all relevant information (in the form of structured data, documents, and images) in different phases, thus allowing an immediate comparison between what is planned (in terms of time, costs, managers and operators, materials, and processes) and what is carried out, also keeping track of all previously closed activities and then generating a detailed history of the interventions for each component of the Asset.

It is possible, therefore, to implement the information relating to maintenance interventions (scheduled, in progress, and already carried out) and to calculate some useful indicators for quick detection of delays (“Variance in time to start work” and “Variance in the duration of work”) and/or misalignments between the estimated costs and actually incurred costs (“Cost variance,” calculated as a difference and as a percentage ratio of incurred costs to estimated costs).

Within the section, support tools are also available for the preparation of the metric-estimative calculation of the activities (interventions or inspections) in the different phases (project/execution) and the archiving of sampling and related analysis results (Figure 5).



Stima frequenza interventi manutenzione

Tabella per la determinazione dell'intervallo di tempo fra due successivi interventi che minimizza i costi complessivi di manutenzione

n° (anni)	C(H) (nm/cc)	R (m/anno)	VdS (cm/s)	conc. SO_2 (microgr/mc)	VdN (cm/s)	conc. HNO_3 (microgr/mc)

Numero anni * 0

Prezzo (€) *

Variabili del differenziale della Formula di Lipfert (modello aggiornato)

n° (anni)	dC(H) (nm/cc)	dR (m/anno)	dVdS (cm/s)	dC(SO_2) (microgr/mc)	dVdN (cm/s)	dC(HNO_3) (microgr/mc)

n° (anni)	Q (micron/anno)	n°·Q (micron)	dQ (micron/anno)
	Q = 18,8 + 0,016·C(H) + R·0,018·(VdS·(SO_2) + VdN·(HNO_3)) [la Letteratura individua un andamento nel tempo della Q descritto dall'equazione: Q=k·t^(1/2)]		dQ = 0,016·R·dC(H))+0,016·C(H) +dR + 0,18·VdS·dC(SO_2) + 0,18·C(SO_2)·dVdS + VdN·dC(HNO_3) + C(HNO_3)·dVdN

n° (anni)	Z	Z'	n
	Costo per micron di materiale da rimettere in opera Z=p·n°·(Q/-dQ) (€)	Costo dell'intervento se effettuato con cadenza "n°" per "m" anni Z'=Z·m/n° (€)	Calcolo dell'intervallo di tempo fra due successivi interventi di manutenzione che minimizza i costi nel periodo di programmazione "m" fissato (ricavato individuando il punto di minimo della funzione A= f(n) = costo complessivo di manutenzione) n= (m·Z'/Z)^(1/2) (anni)

Figure 5. Screens related to the module that implements the predictive model for the economic evaluation of maintenance interventions (developed by 'Sapienza' University of Rome).

Summary

The Decision Support System developed is configured as an articulated tool of analysis and investigation tools. There are two main macro areas:

- One dedicated to controlling and monitoring which, based on data from near-real-time monitoring networks, on automatically calculated indicators, and on the data resulting from verification and maintenance activities, brings to the attention of the operators responsible for all alert situations with the relative severity levels. It also provides systems for visualization and measurement of the geometries of the Asset and the context in which it is inserted, systems for storing and consulting information, structured and not (documents of various kinds such as PDF, images, videos, etc.). It permits planning, managing, and monitoring of ordinary and extraordinary maintenance activities, making it possible to monitor the progress and notify anomalous situations (delays, expected costs overruns, changes in the way interventions are performed).
- The second macro area allows more in-depth analysis of historical data series, not only using the data taken into account by the controlling and monitoring system, but inte-

grating all the information provided both by complex indicators (example: degradation data, number and type of interventions, etc.) and by data from verification and maintenance activities. It integrates the implementation of a predictive model for the economic evaluation of maintenance interventions developed by "Sapienza" University of Rome.

Conclusions

The platform was used to support the Project's experimentation activities on selected use cases for cataloguing, monitoring of microclimatic and environmental parameters, 2D-3D data management and planning and recording of interventions. The evaluation by users of the platform was positive, emphasising its extreme usefulness and ease of use.

All this suggests that in the near future, on the one hand an expansion of the number and information of the cultural assets surveyed, and on the other hand the involvement of an increasing number of organisations and institutions as users of the platform.

Acknowledgements

The SCN_00520 project supported by MIUR is acknowledged.

We thank all the operative units of the project for the contributions provided, useful for the implementation of the technology platform.

References

Blais F., *Review of 20 years of range sensor development*, Journal of Electronic Imaging, vol. 13, 1 (2004), pp. 231–240.

Camuffo D., *Microclimate for Cultural Heritage Conservation, Restoration, and Maintenance of Indoor and Outdoor Monuments*, Elsevier (2014), ISBN 978-0-444-63296-8.

D. Lgs.42/2004, Codice dei beni culturali e del paesaggio, ai sensi dell'articolo 10 della legge 6 luglio 2002, n. 137.

Foramitti H., *Mesures de sécurité et d'urgence pour la protection des biens cul-turels*, ICCROM (1972).

UNI 8290-1, *Edilizia residenziale. Sistema tecnologico. Classificazione e terminologia*, Ente Nazionale Italiano di Unificazione, Milano, (1981).

UNI-EN 10829, *Beni di interesse storico e artistico - Condizioni ambienta-li di conservazione - Misurazione ed analisi*, Ente Nazionale Italiano di Unificazione, Milano, (1999).

UNI-EN 15757, *Conservazione dei Beni Culturali - Specifiche concernenti la temperatura e l'umidità relativa per limitare i danni meccanici causati dal clima ai materiali organici igroscopici*, Ente Nazionale Italiano di Unificazione, Milano, (2010).

UNI-EN 16242, *Conservazione dei beni culturali - Procedure e strumenti per misurare l'umidità dell'aria e gli scambi di vapore tra l'aria e i beni culturali*, Ente Nazionale Italiano di Unificazione, Milano, (2013).

Angela De Bonis
Department of Science (DiS), University of Basilicata, Potenza
Roberto Teghil
Department of Science (DiS), University of Basilicata, Potenza

Laser spectroscopy in cultural heritage and archeology: focus on Raman and LIBS techniques

Abstract

The analysis of artifacts of artistic of archaeological interest requires the use of non-invasive diagnostic techniques, which allow in situ analysis and which, if necessary, can provide indications for the safeguarding, restoration and protection of the manufacts. In this context, the possibility of using laser radiation as an excitation source has allowed the development of particularly important diagnostic technologies. In fact, laser spectroscopies are non-destructive or micro-destructive diagnostics, can be resolved in the three dimensions of space and do not require any manipulation of the sample under examination. Recently, the design and diffusion of portable instrumentations has further expanded their field of use. In our analysis we will focus in particular on the description of the most recently developed laser spectroscopy technique (Laser Induced Breakdown Spectroscopy (LIBS)) and we will show how the combined use of LIBS and micro-Raman spectroscopy can provide a detailed characterization of the elemental and molecular composition of the corrosion patina of bronze artifacts.

Keywords

Micro-Raman, Laser Induced Breakdown Spectroscopy (LIBS), bronze, patina, femtosecond.

Riassunto

La caratterizzazione di manufatti di interesse artistico o archeologico richiede l'utilizzo di tecniche diagnostiche non invasive, che, eventualmente, consentano l'analisi in situ e che, al bisogno, possano fornire indicazioni per la salvaguardia, ripristino e tutela del bene. In questo contesto, la possibilità di utilizzare una radiazione laser come sorgente di eccitazione, ha permesso lo sviluppo di tecnologie diagnostiche di particolare rilievo. Infatti, le spettroscopie laser consentono di effettuare analisi non distruttive o micro-distruttive, risolte in tutte e tre le dimensioni dello spazio e non richiedono alcuna manipolazione del campione in esame. Recentemente, la progettazione e diffusione di strumentazione portatile ha ampliato ulteriormente il loro campo di utilizzo. Nella nostra analisi ci soffermeremo in particolare sulla descrizione della tecnica di spettroscopia laser di più recente sviluppo (Laser Induced Breakdown Spectroscopy (LIBS)) e mostreremo come l'utilizzo combinato della LIBS e della spettroscopia micro-Raman sia in grado di fornire la dettagliata caratterizzazione della composizione elementare e molecolare della patina di corrosione presente su manufatti bronzei.

PAROLE CHIAVE
Micro-Raman, Laser Induced Breakdown Spectroscopy (LIBS), bronzo, patina, femtosecondo.

Introduction

The modern approach for a complete characterization of archeological artifacts involves the combined use of several analytical methods and techniques. When fragile and rare artifacts are analyzed, more attention has to be paid during the experiments because of their fragile structure, therefore it is necessary to use appropriate techniques that, alone or in combination, can provide as much as possible exhaustive information, preserving their integrity and minimizing their damage. Moreover, an archeological object may present inhomogeneity in its chemical composition, due to the alterations related to the burial conditions and could present a very rough surface. Due to these aspects, space resolved analytic methodologies have a relevant role in archaeometric studies.

In the last decades, the featuring characteristics of laser sources have been exploited in order to develop spectroscopic methodologies that offered new opportunities to study and characterize the molecular and elemental composition of solid and liquid samples. In fact, laser, a monochromatic, intense, coherent and directional source of light, can be used as an excitation source for non destructive or micro-destructive schemes of analysis, also for remote characterization. The interaction of the laser beam with a surface may cause different phenomena (such as light absorption, scattering and surface ablation) depending on the incoming power for surface unit (irradiance). In laser spectroscopies, the laser source excites the atoms or molecules in the sample, which then emit and/or scatter light at specific wavelengths. By analyzing the wavelengths of this emitted/scattered light, information can be obtained about the chemical composition and structure of the sample. Laser techniques were used to identify pigments, dyes, and other materials used in the creation of cultural heritage objects, as well as to study their degradation over time. Furthermore, laser spectroscopies are a valuable tool for conservation and preservation efforts, as they allow for detailed analysis without damaging or altering cultural heritage manufacts, finally, as microanalytical and space resolved techniques, they provide a new approach for the study of precious and fragile objects.

Among the several laser spectroscopies, Raman, frequently combined with an optical microscope, and Laser Induced Breakdown Spectroscopy (LIBS) are the two laser methodologies most frequently considered for diagnosis of archeological artifacts. (Aramendia 2019, Giakoumaki 2006).

Micro-Raman spectroscopy is a non-destructive technique that involves the use of a laser to excite the sample, the scattered light is then analyzed to identify the molecular bonds and crystal structure of the material. This well-established technique can provide information about the composition and structure of a variety of materials, including minerals, pigments, and organic materials such as bone, ivory, and textiles. More recently, research has been devoted to the application of Raman imaging for the study of the cross section of microsamples of archeological artifacts or artistic paintings (Aramendia 2019).

Laser-induced breakdown spectroscopy (LIBS) is a micro-destructive technique that involves the use of a high-energy pulsed laser to create a plasma on the surface of the sample. The laser induced plasma emits light that is then analyzed to determine the elemental composition of the material. LIBS can provide information about the presence and relative abundance of elements in the sample, which can help to identify the origin and manufacturing techniques of the artifact, as well as the constituent materials. This technique provides a rapid and accurate analysis with minimal sample preparation and with minimal damage to the artifact. Light elements (such as C, B, H, N and O), that are hard to quantify by means of well-established analytical techniques such as SEM-EDS and XRF, are easily measured in LIBS experiments.

Both micro-Raman and LIBS techniques have emerged in the past years as very promising techniques for the analysis and characterization of a broad variety of objects of cultural heritage including painted artworks, icons, polychromes, pottery, sculpture, metal, glass, and stone objects and can also be used to detect surface coatings, degradation products, and other changes in the material over time. Most of the advances in the application of laser spectroscopies to cultural heritage studies came from the increasing use of portable instrumentation for in situ analysis. Recently, prototype portable instruments (Integrated Laser System ILS-ENEA) that can integrate Raman and LIBS spectroscopies has been successfully applied to the stratigraphic characterization of multilayered ceramics and alloys at a distance of several meters (Fantoni 2019).

Recently the confocal microRaman spectroscopy has been proposed as a powerful tool for nondestructive cross sectional analysis of layered objects such as paintings or degraded surfaces. On the other hand, LIBS allows the qualitative and quantitative elemental analysis of light elements. Combining information obtained by Raman and LIBS experiments Aramendia et al. (Aramendia 2018) demonstrated that it is possible to determine the concentration of hydrated and non-hydrated mineral phases in marble samples with and without a patina of calcium oxalate.

Considering metallic finding, the archaeometric studies are devoted to acquire knowledge on alloy composition (major, minor and if possible trace elements), metallographic features and corrosion products, with the aim of formulating hypotheses on the production area or classifying the analyzed objects. Moreover, corrosion process and degradation phenomena should be studied in order to make possible the more adequate strategies of restoration and conservation for these metallic artifacts.

In the following, the basic principles and the main advantage of the LIBS technique will be presented in relation to the fields of characterization and conservation of cultural heritage artifacts and some examples will be given.

Finally, a case of study will be presented where micro-Raman and LIBS spectroscopies have been used to fully characterize a corroded bronze object.

Laser Induced Breakdown Spectroscopy

LIBS has become popular among other atomic emission spectroscopy methods in connection with the invention and development of lasers, but its intense applications took place only in the last three decades, when the more advanced instruments were introduced. In comparison to other analytical techniques, LIBS experimental set up is very simple and includes:

- a laser source: the most widely used lasers in LIBS experiments are nanosecond (ns) pulsed sources that provide wavelengths in the spectral range from Uv to NIR. The advantages and drawbacks of femtosecond (fs) pulsed sources with respect to ns ones in LIBS experiments have been discussed by some researchers (Almaviva 2014, De Bonis 2014).
- a spectrometer equipped with a time resolved detector;
- some focusing optics;
- a computer for data acquisition.

The scheme of a LIBS set up is shown in figure 1.

During the brief interaction of a focused laser pulse with a solid surface, a process known as laser ablation occurs with the atomization, ionization and evaporation of small amounts of matter (from nanograms to micrograms). After a few nanoseconds, the formation of a microplasma plume just above the sample surface can be observed. The hot plasma cools down quickly and, during the cooling process, the electrons and ions recombination results in emission of spectral lines of characteristic wavelengths. The plasma emission can last a few microseconds and is collected and focused in the spectrometer, resulting in a spectrum where the emission peaks at characteristic wavelength reflects the elemental composition of the target. It is noted that up to some hundreds of ns after the laser pulse, the emission of the laser induced plasma is dominated by an

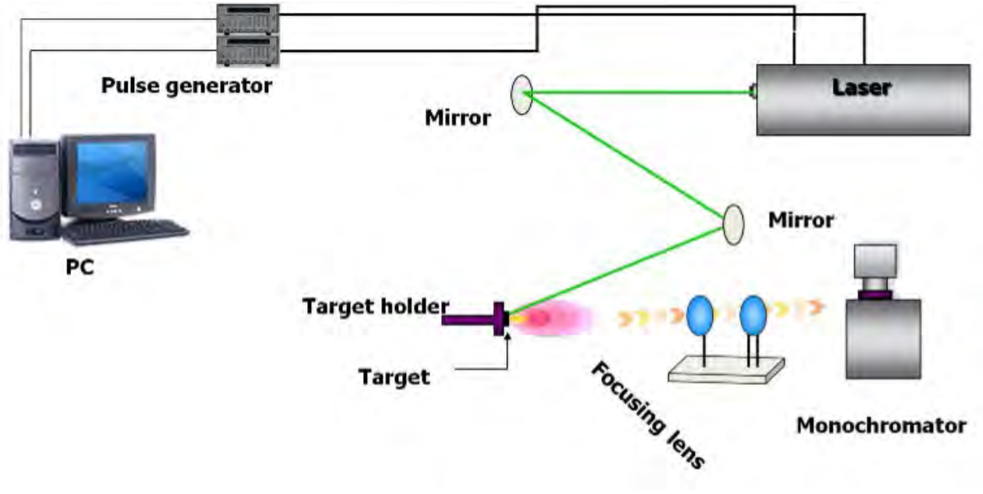


Figure 1. Experimental set up for LIBS analysis.

unstructured spectral continuum. As this continuum decays, the sharp atomic emission lines are visible. Therefore, it is essential to select the optimal delay with respect to the laser pulse and the optimal time gate width to register the emission spectrum in the best conditions. Moreover, the choice of some experimental conditions (such as laser pulse length and energy, repetition rate and wavelength) depends on the sample composition and geometry and must be defined for each experiment. When optimal conditions are found, LIBS analysis becomes very fast.

The use of LIBS as quantitative analysis is less straightforward. The peak intensity or area of the emission lines can be associated with the concentration of specific elements in the analyzed surface, but, the physic-chemical properties of the samples can significantly affect the ablation dynamics, the plasma composition, the plasma temperature and in turn, the intensity of LIBS signals. In fact, the intensity of the emitted spectral lines, that can be used for quantitative analysis, are related both to the amount of the corresponding element in the plasma plume and to the plasma properties and the relationship between the experimental intensity of the spectral lines and the amount of the relative elements in the analyzed sample is quite complex. Some conditions need to be fulfilled: first of all, the laser ablation has to be stoichiometric, i.e. the composition of the plasma should reflect the material composition, secondly the plasma should be optically thin, i.e. self-absorption effects should be neglected, and finally the Local Thermodynamics Equilibrium (LTE) conditions should be respected. The description of this last condition is beyond our scope, the interested reader can refer to detailed reviews. (Gaudiuso 2010, Cristoforetti 2010).

When the previously described conditions are fulfilled, the intensity of each spectral line can be described as

$$I_{ul} = \frac{N_{0,at}\, g_u\, A_{ul}\, h\nu_{ul}}{Z(T)} \exp\left(\frac{E_u}{kT}\right)$$

where:

- $N_{0,at}$ = number of atoms,
- T = plasma temperature,
- I_{ul} = spectral line intensity for the transition between two electronic levels (u= upper, l=lower),
- g_u = higher level degeneration,
- A_{ul} = spontaneous emission Einstein coefficient,
- ν= photon frequency,
- E_u = higher level energy,
- Z(T) = partition function.

For reliable quantitative analysis, different approaches have been proposed. The most frequently applied approaches are:

- the use of Calibration Curves, using samples with known composition whose matrices are very similar to the unknown sample;

- the Calibration-Free approach, that requires the precise determination of the plasma parameters (electron temperature and electron density) and the fulfillment of some theoretical assumptions (Hermann 2023, Wang 2021).

Finally, we have to consider the role of the laser pulse length on LIBS experiments. The first steps in the LIBS analysis are the interaction of a laser source with a solid surface, the local ablation of the sample and the formation of a laser induced plasma. All these processes are deeply affected by the laser pulse length. First of all, nanosecond and femtosecond laser sources give different mechanisms of light-matter interaction. By using a nanosecond laser source, the presence of thermal effects during the ablation step causes the local melting of the sample. When a layered object is studied, the mixing of layers with different compositions can take place. On the other hand, by using ultrashort (fs) laser sources, the thermal effects can be neglected, without melting of the solid target, and the possibility to ablate a layered object in a controlled way. The lower ablation rate and the absence of thermal effects gives minimal damage to the artifact for fs with respect to ns LIBS experiments. Secondly, the ns laser pulse can interact with the laser induced plasma, with its re-heating and the consequently generation of more intense spectral lines. Considering the combination of the effects described, LIBS experiments carried out with ns laser sources allow to obtain reproducible and intense atomic emission spectral lines, on the other hand by using a fs laser source it is possible to perform a depth profiling analysis with minimal damaging of artifact.

Since 2000, LIBS has been more and more applied to the field of cultural heritage mainly for materials characterization, recognition of fakes, conservation, indirect dating and, more recently, it has an increasing place for in situ analysis for archeological application or during the restoration work (Spizzichino 2014).

One of the first applications of LIBS for the characterization of a layered polychrom has been reported by Castillejo *et al.* (Castillejo 2000). They studied a fragment of a gilded altarpiece from the church of Escatron, Zaragoza, Spain, characterizing the successive layers of pigments in the painted structure (Castillejo 2000).

A ns laser source, at wavelength of 1064nm, was used for the identification of pigments used in the realization of a fresco from the archeological area of Pompei. The authors considered the intensity ratio of the emission lines of selected elements as possible indicators for the pigments recognition (Caneve 2010).

LIBS experiments carried out with Uv laser source (at wavelength of 266nm) is a potential tool for varnish removal in painting restoration. The recognition of specific molecular emission bands can be a marker for organic varnish material, and by carefully selecting the appropriate fluence it is possible to obtain a fine depth resolution in material removal, obtaining useful information in painting cleaning and restoration (Staicu 2016).

For the first time, the capability of LIBS for the analysis of submerged materials was demonstrated by Guirado *et al.* (Guirado 2012). The laser radiation delivered through an optical fiber was used to characterize some organic and inorganic archaeological artifacts without altering the archeological site.

Finally, it is interesting to report the study of Kasem *et al.* (Kasem 2011) that used LIBS technique to characterize some archeological bone samples obtaining information about the customs and dietary habits of ancient Egyptians.

As qualitative elemental analytical technique, LIBS presents many advantages such as:

- sampling: the technique can be used in situ and there is no need of pretreatment or geometrical requirement for the sample;
- simultaneous multielemental analysis: also light elements can be measured by LIBS analysis;
- non-contact analysis: it is possible to study harsh or fragile objects;
- depth profile analysis: successive LIBS spectra obtained with a few pulses on the same point give the stratigraphic composition of layered samples;
- fast measurements speed of analysis, with the possibility to analyze a large number of objects in a short time.

Despite these advantages, LIBS has some drawbacks:

- a low limit of detection (LoD): in the order of ppm:
- poor reproducibility: mainly due to the matrix effect;
- micro-destructiveness: a portion of the analyzed object, though very small, must be removed;
- complexity of quantitative analysis.

Considering the low LoD, to enhance the intensity of the emission signals, some modifications of the LIBS experimental set up have been proposed (Kan 2022).

A case of study: the corrosion of bronze

The study of the chemical degradation phenomena of ancient metallic objects can provide useful information for the evaluation of the state of conservation of objects and for the understanding of degradation mechanisms. The corrosion phenomena are redox processes that cause the deterioration and degradation of the material properties and modify the chemical composition of the sample by introducing elements coming from the external environment.

Due to its good ductility, mechanical strength and bright color, copper and its alloys have been widely used from the Bronze Age, for this reason, the conservation and protection of bronze objects from corrosion phenomena are considered of primary necessity for the study of our history.

Bronze is an alloy of copper, tin and, in some cases, lead, which on the surface is easily altered, forming compact layers of corrosion products, which generally take the name of "patina" and which offer partial protection to the metal substrate. The characterization of the patina, and the understanding of the mechanism of its formation, is of fundamental importance to define the possible conservation and possible removal treatments of the corrosion products, which are encrusted and stratified on the metal surface. The corroded bronze artifacts are greenish or brownish green due to the presence on their surface of copper (II) compounds. These degradation products cover an inner cuprous layer that is directly in contact with the alloy surface, usually.

The cuprite (CuO) layer is responsible for the initial formation of a patina and for the decuprification process that consists in the selective dissolution of copper compounds and the enrichment in low solubility tin compounds of the external surface of the artifact. The differential migration of elements creates a concentration gradient through the corrosion layer of the bronze alloys. Furthermore, the environment influences the chemistry of the degraded layer: bronze objects buried in soils are covered by a malachite layer (copper carbonate), whereas for objects exposed to air or seawater environment the enrichment in brochantite (copper sulfate) and atacamite (copper chloride) species has been observed, respectively.

A multidisciplinary approach that includes fs LIBS and micro-Raman spectroscopies will allow us to understand the whole corrosion process, obtaining information about the corrosion depth and the chemical composition of the corroded layer.

A bronze ingot of known composition (Cu-Sn 88-12 wt%) has been artificially corroded with the wet test (Kesternich Corrosion test) in an Erichsen cyclic corrosion chamber (Mod.519/AUTO), in order to simulate the exposure of bronze artifacts to natural acid rains (figure 2). Due to the corrosion treatment, a greenish patina was formed on the surface of the ingot.

Figure 2. Bronze ingot before and after the corrosion test.

The LIBS equipment used to analyze the corroded bronze is composed of a fs laser source, NdGlass laser (l=527nm, 10Hz, 3mJ, 250fs), a spectroscopic system, a pulse generator and a target holder. An optical system consisting of mirrors and focusing lenses was used to convey the plasma emission directly in an optical fiber connected to the spectrograph entrance. The depth profiling of the corroded ingot has been obtained considering the emission spectrum with increasing the number of laser shots on the same point.

In figure 3 is reported a typical spectrum obtained in the 278-290 nm region, where the emission lines of Cu+, Cu and Sn species are clearly visible. The emission lines at 282.35nm (Cu) and 283.94nm (Sn) have been considered to evaluate the Cu/Sn ratio.

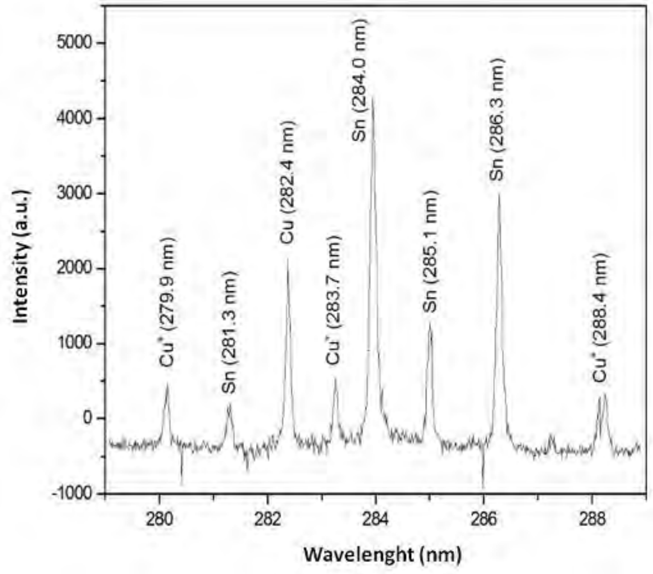


Figure 3. LIBS analysis of the corroded bronze ingot.
The emission lines in the 278-290nm region are shown.

Considering the Cu/Sn ratio, with increasing the number of laser shots (figure 4) it was possible to observe their elemental distribution in the patina and in the bronze. In the first layer of the patina it is possible to observe the higher concentration of copper with respect to the bronze composition, suggesting the formation of degradation compounds such as brochantite, antlerite, cuprite and so on. With the increase of the number of laser shots, the Cu/Sn ratio, deeply decreased due to the well-known decuprification effect. Finally, after about 30 laser shots, the patina was removed and the Cu/Sn ratio rose up to a constant value corresponding to the bulk composition of the bronze.

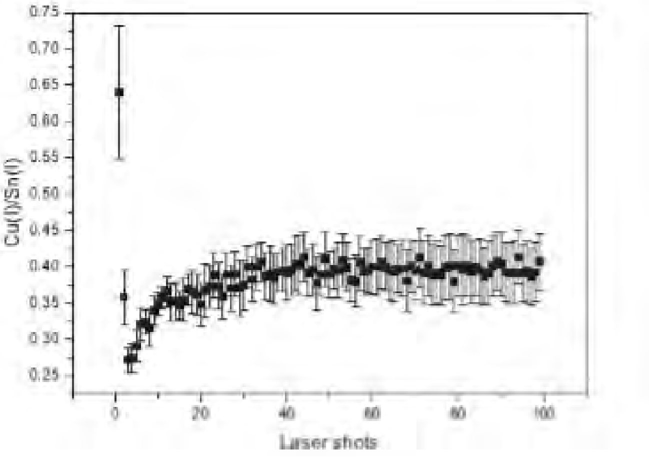


Figure 4. Cu/Sn composition profile obtained by fs LIBS.

Raman spectra were acquired by the LabRam HR800 (Horiba) instrument, equipped with a He-Ne laser source (632.8nm) and with an Olympus microscope (with 10x, 50x and 100x objectives). The laser power has been fixed to 20mW in order to minimize the target degradation.

Micro-Raman analysis gets information of the mineralogical composition of the patina. The observation of the altered bronze surface shows the presence of areas with different colors, suggesting the presence of different corrosion compounds. In particular, the large majority of the surface presents green crystals, whereas some zones display a brownish color. The Raman spectrum acquired in the greenish region can be referred to brochantite ($Cu_4SO_4(OH)_6$) and chalcantite ($CuSO_4{\cdot}5H_2O$) crystals, whereas in the brownish zone, signals that can be referred to antlerite ($Cu_3SO_4(OH)_4$) have been observed.

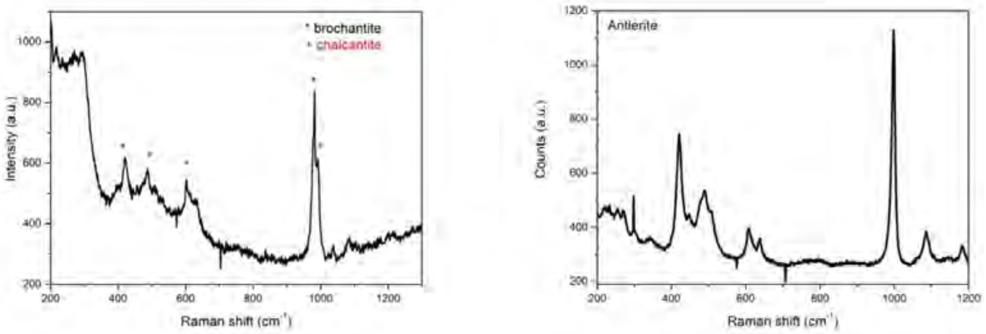


Figure 5. Raman spectra acquired in two different area of the corroded bronze ingot. The spectral features of brochantite, chalcantite and antlerite are present.

Conclusions

We have shown how the combined use of LIBS and Raman spectroscopy represents a valid approach for the characterization of artistic artifacts and archeological findings and to acquire a detailed knowledge of the investigated object, to understand the manufacture of archeological findings or to suggest conservation strategies. A case of study has been reported showing the complementary information that can be obtained by LIBS and microRaman analysis for the characterization of the corrosion patina of bronze objects. The higher copper concentration in the first layers of the patina with respect to the nominal composition of the bronze ingot suggests the formation of degradation compounds whose mineralogical composition has been confirmed by Raman analysis.

References

S. Almaviva – R. Fantoni – L. Caneve – F. Colao – L. Fornarini – A. Santagata – R. Teghil, *Use of ns and fs pulse excitation in laser-induced breakdown spectroscopy to improve its analytical performances: A case study on quaternary bronze alloys*, «Spectrochimica Acta Part B: Atomic Spectroscopy». 99 (2014), pp. 185-192.

L. Angeli – C. Arias – G. Cristoforetti – C. Fabbri – S. Legnaioli – V. Palleschi – G. Radi – A. Salvetti – E. Tognoni, *Spectroscopic Techniques Applied to the Study of Italian Painted Neolithic Potteries*, «Laser Chemistry ». 2006 (2006), 61607.

J. Aramendia – L. Gómez-Nubla – S. Fdez-Ortiz de Vallejuelo – K. Castro – G. Arana – J. M. Madariaga, *The combination of Raman imaging and LIBS for quantification of original and degradation materials in Cultural Heritage*, «Journal of Raman Spectroscopy ». 50 (2019), pp. 193-201.

A. Botto – B. Campanella – S. Legnaioli – M. Lezzerini – G. Lorenzetti – S. Pagnotta – F. Poggialini – V. Palleschi, *Applications of laser-induced breakdown spectroscopy in cultural heritage and archaeology: a critical review,* «Journal of Analytical Atomic Spectrometry». 34 (2019), pp. 81-103.

M. Castillejo - M. Martin - D. Silva - T. Stratoudaki - D. Anglos - L. Burgio - R.J.H. Clark, *Laser induced breakdown spectroscopy and Raman microscopy for analysis of pigments in polychromes*, «Journal of Cultural Heritage». 1 (2000), pp. 297-S302.

L. Caneve - A. Diamanti - F. Grimaldi - G. Palleschi - V. Spizzichino - F. Valentini, *Analysis of fresco by laser induced breakdown spectroscopy,* «Spectrochimica Acta Part B: Atomic Spectroscopy». 65 (2010), pp. 702-706.

G. Cristoforetti - A. De Giacomo - M. Dell'Aglio - S. Legnaioli - E. Tognoni - V. Palleschi - N. Omenetto, *Local Thermodynamic Equilibrium in Laser-Induced Breakdown Spectroscopy: Beyond the McWhirter criterion*, «Spectrochimica Acta Part B: Atomic Spectroscopy». 65 (2010), pp. 86-95.

A. De Bonis – B. De Filippo – A. Galasso – A. Santagata – A. Smaldone – R. Teghil, *Comparison of the performances of nanosecond and femtosecond Laser Induced Breakdown Spectroscopy for depth profiling of an artificially corroded bronze,* «Applied Surface Science». 302 (2014), pp. 275-279.

A. De Giacomo – M. Dell'Aglio – O. De Pascale – R. Gaudiuso – A. Santagata – R. Teghil, *Laser Induced Breakdown Spectroscopy methodology for the analysis of copper-based-alloys used in ancient artworks*, «Spectrochimica Acta Part B: Atomic Spectroscopy». 63 (2008), pp. 585-590.

V. Detalle – X. Bai, *The assets of laser-induced breakdown spectroscopy (LIBS) for the future of heritage science*, «Spectrochimica Acta Part B: Atomic Spectroscopy». 191 (2022), 106407.

R. Fantoni - S. Almaviva - L. Caneve - F. Colao - M. Ferri De Collibus - L. De Dominicis - M. Francucci - M. Guarneri - V. Lazic - A. Palucci, *In situ and remote laser diagnostics for material characterization from plasma facing components to Cultural Heritage surfaces*, «Journal of Instrumentation». 14 (2019), C07004.

R. Gaudiuso - M. Dell'Aglio - O. De Pascale - G.S. Senesi - A. De Giacomo, *Laser Induced Breakdown Spectroscopy for elemental analysis in environmental, cultural heritage and space applications: a review of methods and results*, «Sensors». 10 (2010), pp. 7434-7468.

A. Giakoumaki - I. Osticioli - D. Anglos, *Spectroscopic analysis using a hybrid LIBS-Raman system*, «Applied Physics A». 82 (2006), pp. 537-541.

S. Guirado - F.J. Fortes - V. Lazic - J.J. Laserna, *Chemical analysis of archeological materials in submarine environments using laser induced breakdown spectroscopy. On site trials in the Mediterranean Sea,* «Spectrochimica Acta Part B: Atomic Spectroscopy». 74-75 (2012), pp. 137-143.

J. Hermann – C. Gerhard – M. Burger – V. Craciun – F. Pelascin, *Progress in calibration-free laser-induced breakdown spectroscopy*, «Spectrochimica Acta Part B: Atomic Spectroscopy». 200 (2023), 106595.

Z. H. Khan - M. Hedayet Ullah - Bulu Rahman - A.I. Talukder - Md. Wahadoszamen - K. M. Abedin - A. F. M. Y. Haider, *Laser-Induced Breakdown Spectroscopy (LIBS) for Trace Element. Detection: A Review*, «Journal of Spectroscopy». (2022), 3887038.

M.A. Kasem - R.E. Russo - M.A. Harit, *Influence of biological degradation and environmental effects on the interpretation of archeological bone samples with laser induced breakdown spectroscopy*, «Journal of Analytical Atomic Spectrometry». 26 (2011), pp. 1733-1739.

G. S. Senesi – R. S. Harmon – R. R. Hark, *Field-portable and handheld laser-induced breakdown spectroscopy: Historical review, current status and future prospects*, «Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy». 175 (2021), 106013.

A. Smaldone – A. De Bonis – A. Galasso – A. Guarnaccio – A. Santagata – R. Teghil, *Inverse calibration free fs-LIBS of copper-based alloys*, «Zeitschrift fur Physikalische Chemie». 230 (2016), pp. 1201-1217.

V. Spizzichino -R. Fantoni, *Laser Induced Breakdown Spectroscopy in archeometry: a review of its application and future perspectives*, «Spectrochimica Acta Part B: Atomic Spectroscopy». 99 (2014) pp. 201-209.

A. Staicu - I. Apostol - A. Pascu - I. Urzica - -M.L. Pascu - V. Damian, *Minimal invasive control of painting cleaning by LIBS*, «Optical & Laser Technology». 77 (2016), pp. 187-192.

M. Veneranda - N. Prieto-Taboada - S. Fdez-Ortiz de Vallejuelo - M. Maguregui - H. Morillas - I. Marcaida - K. Castro - F.J. Garcia-Diego - M. Osanna - J.M. Madariaga, *In-situ multianalytical approach to analyze and compare the degradation pathways jeopardizing two murals exposed to different environments (Ariadne House, Pompeii, Italy)*, «Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy». 203 (2018), pp. 201-209.

Z. Wang - M.S. Afgan - W. Gu - Y. Song - Y. Wang - Z. Hou - W. Song - -Z. Li, *Recent advances in laser induced breakdown spectroscopy quantification: from fundamental understanding to data processing*, «Trends in Analytical Chemistry». 143 (2021), 116385.

Laura Scrano
Department of European and Mediterranean Cultures (DiCEM)
University of Basilicata, Matera, Italy

Bio-strategies for the conservation of lithic and metallic heritage

SUMMARY

The stone material, the main constituent of historic buildings and monuments, and the metal finds deriving from archaeological excavations represent a part of our cultural heritage. Both are subject to deterioration linked to climatic conditions and habitats for various biota capable of colonizing surfaces and fissures, inducing aesthetic and structural damage. Usually, the organisms responsible for biodeterioration are controlled by synthetic chemical products, which, however, can represent a serious problem for the environment, the cultural heritage, and the operators' health. To contribute to the protection of the environment and health, an ecological approach was tested. Extracts of *Solanum nigrum L.*, *Moricandia arvensis L.*, spontaneous plants, and secondary metabolites contained in the culture broth of fungus *Beauveria bassiana Will.* were used for environmentally friendly cleaning of the materials. All the extracts mentioned have shown high efficacy at low concentrations and have proven harmless from an environmental and toxicological point of view.

KEYWORDS

Conservation, stone heritage, metal finds, *Solanum nigrum L.*, *Cornus capitata* and *Moricandia arvensis L.*, *Beauveria Bassiana Will.*

RIASSUNTO

Il materiale lapideo, principale costituente degli edifici storici e dei monumenti e i reperti metallici rivenienti da scavi archeologici rappresentano una parte del nostro patrimonio culturale. Entrambi sono soggetti a deterioramento legato alle condizioni climatiche ma sono, anche, habitat per un'ampia varietà di biota abili nel colonizzare superfici e fessure inducendo danni estetici e strutturali. Solitamente gli organismi responsabili del biodeterioramento sono controllati da prodotti chimici di sintesi che, tuttavia, possono rappresentare un serio problema per l'ambiente, per gli stessi beni culturali e per la salute degli operatori. Nell'ottica di contribuire alla salvaguardia dell'ambiente e della salute è stato sperimentato un approccio ecologico: estratti di *Solanum nigrum L.*, e *Moricandia arvensis L.*, piante spontanee e metaboliti secondari contenuti nel brodo di cultura del fungo *Beauveria bassiana Will.* sono stati adoperati per una pulizia ecocompatibile del materiale. Tutti gli estratti citati, hanno evidenziato alta efficacia a basse concentrazioni e sono risultati innocui dal punto di vista ambientale e tossicologico.

Parole chiave
Conservazione, patrimonio lapideo, reperti metallici, *Solanum nigrum L.*, *Cornus capitata* e *Moricandia arvensis L.*, *Beauveria Bassiana Will.*

1. Introduction

The deterioration of lithic artworks, our precious historical and cultural heritage, is a common problem, and it is a challenge for humanity to protect and preserve them. The deterioration begins when moving the rocks from the quarry and then continues when the asset is exposed to atmospheric agents. Dissolution of calcium carbonate induced by the solvent action of acid rainwater, leaching of exposed surfaces, pH changes, black crusts, saline efflorescence, and sub-florescence (Bell, 1993; Camuffo, 1995; Ordóñez et al., 1997; Papida et al., 2000) are some evident manifestations of deterioration. Biological degradation should not be underestimated, which unfortunately becomes evident only when it is macroscopically visible as proof that a complex ecosystem has already been created, which can damage the asset aesthetically and structurally (De Leo et al., 2012İ; Laiz et al., 2003; Suihko et al., 2007; Jurado et al., 2010; Jurado et al., 2012; Miller et al. 2009). The need to protect the cultural heritage and preserve it for public use has been desired since ancient times: Roman architects had implemented particular construction devices such as roofs or canopies and protective treatments of the walls precisely to achieve the abovementioned purpose (Siegesmund et al., 2002).

Even metallic artifacts, which might seem more resistant to degradation, are very sensitive and fragile. Studies carried out on iron or copper alloy objects found in different environments (on the ground, in cinerary urns, ceramic vases, in an underwater environment) have shown deterioration of a physical type (cracks, cavities) and chemical alteration depending on both the composition of the object (e.g., pure metals or alloys) and from climatic/anthropic factors (Robbiola et al., 1998; Domenech-Carbo, 2010; Robbiola and Portier, 2006; Aparaschivei, 2012; Domenech-Carbo, 2011; Mircea, 2010). For example, outdoors, in the presence of pollutants, rain, etc., the copper alloy finds to develop a patina which, over time, acquires different colors ranging from light green to brownish green, and the products of corrosion fix the color of the patina formed, the main form of degradation (Cano et al., 2010; Wan et al., 2012; Unutulmazsoy et al., 2020; Aromaa et al., 2021. On the other hand, the lead finds show only a slight deterioration since the formation of the protective film of lead oxide and lead carbonates drastically inhibits corrosion (Reale et al., 2012). This effect explains why lead objects found in archaeological sites are usually in good condition. Opposite, lead corrodes severely in wet environments, particularly in the presence of organic acid vapors (Niklasson et al., 2005).

It is evident how essential it is to understand the chemical/physical/atmospheric processes involved before undertaking any conservation work since inappropriate treatments could cause irreversible damage to unique and irreplaceable objects and, in any case, any corrective measure should be more directed towards correct conservation more than to the restoration (Flexer et al., 2015; Costa and Urban, 2005; Balliana et al., 2016).

To be consistent about achieving the objective required by Art. 9 of the Italian Republic Constitution, "The Republic promotes the development of culture and scientific and technical research, protects the landscape and the historical and artistic heritage of the country."

Correct conservation involves cleaning and consolidating the stone/metal cultural asset, possibly in an environmentally friendly way, to meet the need to preserve the environment, health, and cultural heritage.

Traditionally, the control of degradation in general and bio-degradation, in particular, is based on the use of synthetic products, which, unfortunately, over time, have shown a specific negative impact on the environment, health, and, sometimes, on the substrates of the goods treated (Hawks et al., 2010; Schrager et al., 2017).

Therefore, research on the conservation (cleaning and consolidation) of stone and metal assets must focus on using ecological substances/environmentally compatible treatments that comply with the applicable standards and regulations on toxicity and environmental protection (Sharma et al., 2012; Goni and Mazumder, 2019: Young et al., 2008). To this aim, the multidisciplinary research team of the University of Basilicata, made up of chemists, biologists, agronomists, and microbiologists, with the collaboration of researchers from other European universities, has directed the research on the use of natural substances obtained from the metabolic activity of spontaneous plants and microorganisms (bacteria and fungi) diversified treatment depending on whether stone or metal material. The common feature of the natural products used is the high specificity of action, efficacy at low concentrations, rapid decomposition, and non-interference with the constituent material of the work (Ramírez et al., 2005; Szewczyk et al., 2006).

Action on Stone Materials

Natural extracts contain organic molecules not involved in an organism's normal growth and development. These substances, called secondary metabolites, perform functions that are not fully understood, but it has been demonstrated that they play a crucial role in the defense of the plant organism (Agostini-Costa et al., 2012; Chowński et al. 2016).

The recognition of the biological properties of thousands of these molecules has increased the interest in this field to research new drugs, antibiotics, insecticides, fungicides, and herbicides. It has allowed the re-evaluation of the role of bacteria, fungi, and plants, especially in the ecological context.

Each family, genus, and species of different plants/microorganisms produce synergistically active substances that counteract pathogenic attacks (Braga et al., 2005).

Figure 1 shows the secondary metabolites mainly present in *Solanum nigrum L.* and *Moricandia arvensis L.* extracts, while Figure 2 shows the confirmed actions and activities (Marciniak et al., 2019; Spochacz et al., 2021; Berreghioua et al., 2016).

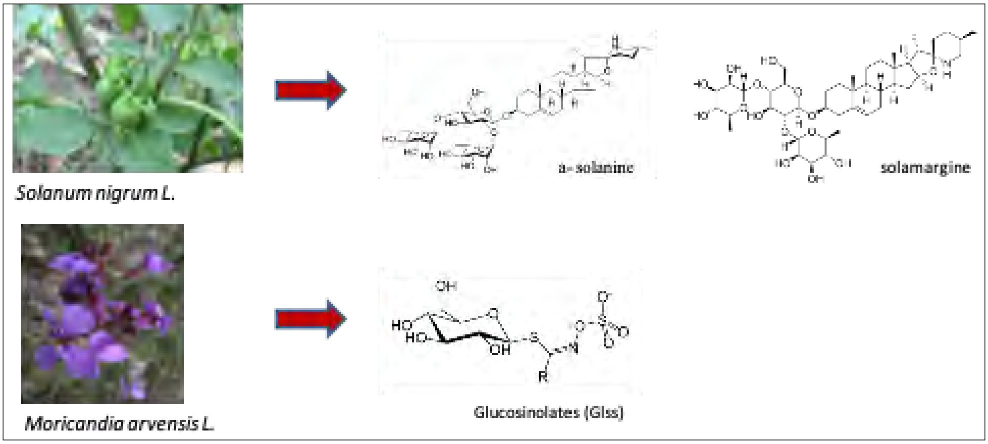


Figure 1. Main metabolites contained in the extracts of *Solanum nigrum L.* and *Moricandia arvensis L.*

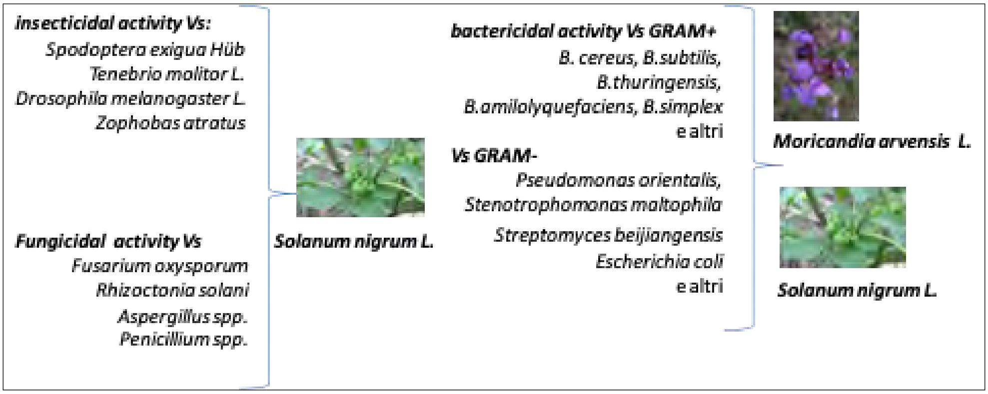


Figure 2. The activity of *Solanum nigrum L.* and *Moricandia arvensis L.* extracts.

Figure 3 shows the effect of cleaning using *Solanum nigrum L.* extract on stone material from Hontoria (Spain) contaminated by numerous biodeteriogenic species (Sasso et al., 2016). Digital image analysis (DIA, data not shown), photosynthetic biomass quantification (data not shown), and confocal laser scanning microscopy (CLSM) were conducted to verify the efficacy of the treatment.

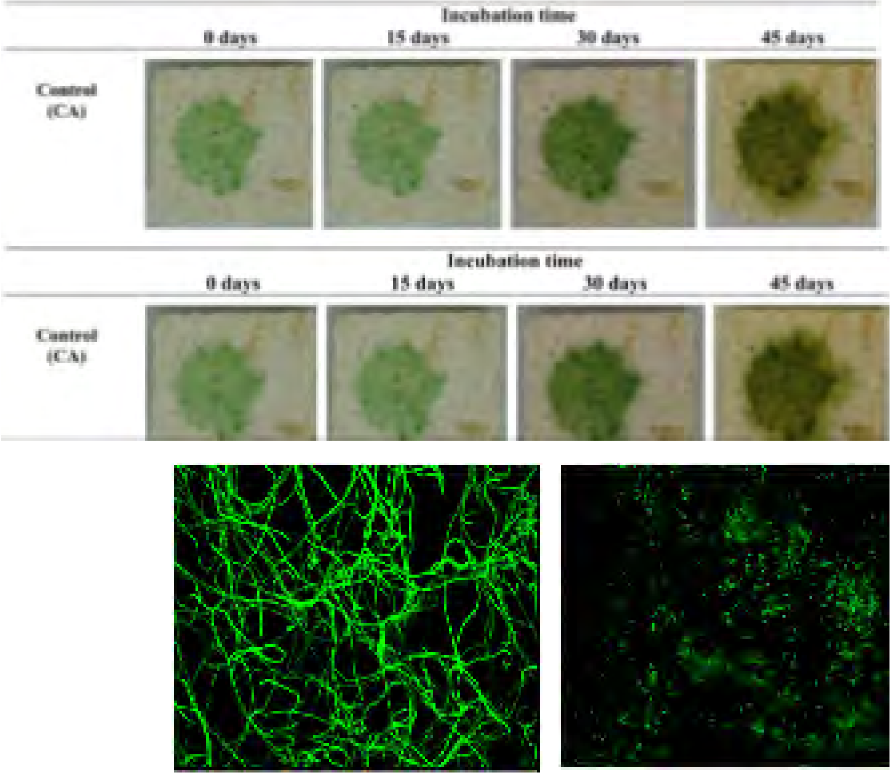


Figure 3. Results of biotreatment on rock samples: (A) visual analysis, (B) CLSM analysis (Sasso et al., 2016).

All the extracts showed and confirmed their great exclusive efficacy towards the entire Gram + bacterial structure sampled and identified on the surface of the stone materials. Gram- bacteria are not sensitive to the action since they are characterized by a cell wall that acts as a selective barrier to substances coming from outside (Sasso et al., 2013; Sasso et al., 2013).

It must be specified that:

- the action of the extracts is not immediate and radically decisive if the biodegradation is advanced
- the extract shows greater effectiveness in the removal than the pure chemical compounds mixed as proof of the synergistic action carried out by minor products contained in the natural mixture (Sasso et al., 2016; Sasso et al., 2013; Sasso et al., 2013; Faraja et al., 2018; Scrano et al., 2020).

The extracts used, subjected to ministerial ecotoxicological tests using the small freshwater crustacean *Daphnia magna Straus* and the bioluminescent bacteria of the *Vibrio fischeri* species, gave negative results confirming the environmental safety of the substances.

Action on Metal cultural finds

Even for archaeological metal artifacts or works of Art, for some time now, many scholars have directed their research towards green cleaning, consolidation, and conservation protocols to protect the assets, the health of the operators, and the environment.

Corrosion is the main form of degradation of metal finds and is intrinsically linked to the environmental context in which they are located. Corrosion products result from electrochemical reactions with environmental contaminants (Figure 4) (Artesani et al., 2020).

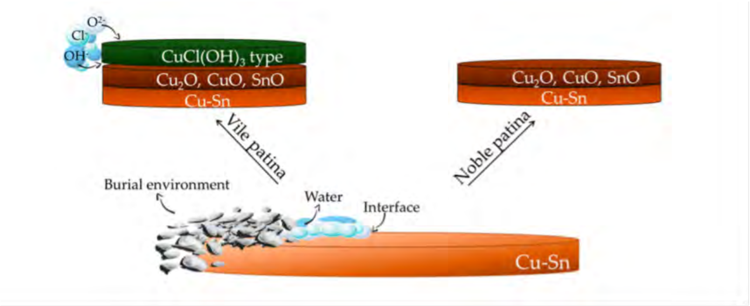


Figure 4. Schematic corrosion process (Artesani et al., 2020).

The patina of corrosion, although considered aesthetically valuable since it tells us the story of the find, very often makes it fragile from the point of view of conservation. Therefore it is necessary to proceed with conservative restoration interventions (Albini et al., 2016). Traditionally, the conservation-restoration methods of artifacts are based on the use of benzotriazole (BTA) as a corrosion inhibitor of copper artifacts and on the subsequent coating with microcrystalline waxes (R21 wax, TeCe Wachs3534F) and acrylic resins (Incralac®) (Brostoff, 2003; Letardi, 2004). The European Chemical Agency (ECHA) has classified this substance as toxic to the environment and health. At the same time, the use of waxes and resins has some disadvantages, such as surface opacity, the need for regular maintenance, and in the case of acrylic resins, the fragility of the film and the difficulty of its removal in case of degradation (Brostoff, 2003; Letardi, 2004).

Therefore, the need to apply eco-friendly conservation methods suggested by nature is evident. Microorganisms, for example, often considered harmful to cultural heritage because they are bio-deteriogens, can also be used for its protection (Gadd, 2010).

The literature reports the ability of some fungal strains to transform metal compounds into highly insoluble and chemically stable metal oxalate complexes, even in acidic conditions. This peculiarity can be exploited not only in agriculture to detoxify copper-contaminated soils but also as a method for the conservation and protection of the surface of artistic and archaeological metal artifacts since the metal corrosion products can be converted into passivating biogenic minerals (oxyhalogenesis), which confer long-term stability of the treated surfaces (Joseph et al., 2017; Joseph et al., 2012; Green et al., 2003; Gadd, 1999). All these results are promoted with different mechanisms by secondary metabolites with chelating properties, including oxalic acid (Figure 5).

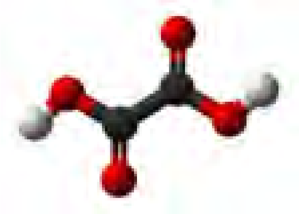


Figure 5. Structure of oxalic acid.

Among the various fungal strains studied in this regard by various researchers (Sayer and Gadd, 1997; Gharieb et al., 2004; Fomina et al., 2005), the species *Beauveria Bassiana Will.* stands out, and in particular, the strain isolated from vineyard soils highly contaminated by copper, a substance widely used in phytosanitary defense in viticulture for the control of the oomycete *Plasmopara viticola* Berl. & De Toni. This strain produces high amounts of oxalic acid as the main component. No other organic acids can create patinas of oxalates without forming carboxylates, as in different fungal strains by converting almost entirely from copper hydroxysulphates and hydroxychlorides to stable copper oxalates (Mazzeo and Joseph, 2004; Ávila-Hernández et al., 2020).

Figures 6 and 7 show the effects of the treatments of copper specimens subjected to artificial corrosion with *Beauveria Bassiana Will.* culture broth and the Transformed Infrared Spectroscopy (FTIR) analysis, which highlights the formation of copper oxalate.

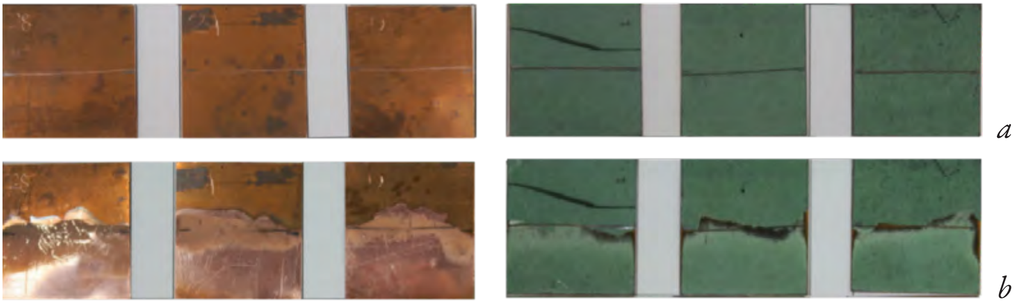


Figure 6. Colorimetric difference between copper specimens before (a) and after (b) treatment with broth culture of *Beauveria bassiana Will.*
Legend: (red) Copper oxalate, (green) copper specimen

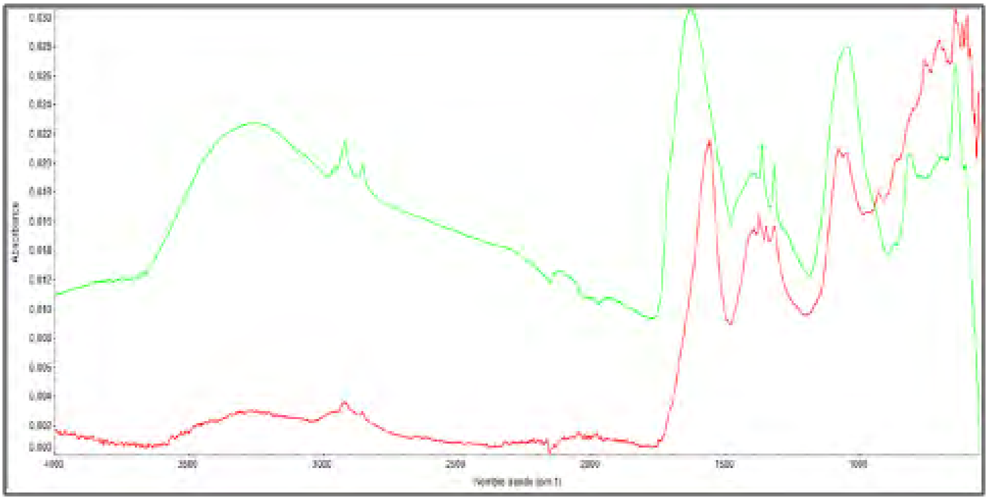


Figure 7. FTIR analysis on sample after treatment with culture broth of *Beauveria Bassiana Will.*

Treatments carried out with filtered culture broth, with culture broth mixed with gel and with commercial oxalic acid at the same concentration as that contained in the culture broth, always on artificially aged copper samples, have not reported results of equal effectiveness.

These results confirm the research of many researchers who have been trying to use green solutions for safeguarding and protecting our historical but also recent heritage (Argyropoulos, 2021).

In addition, it is clear how necessary it is to continue the study on the characterization of even the minor components present in the culture broth, which allows the achievement of the objectives.

Also, in this case, the culture broth w*as* subjected to ministerial ecotoxicological tests using the small freshwater crustacean *Daphnia magna* Straus and the bioluminescent bacteria *Vibrio fischeri* spp., which gave negative results confirming the environmental safety of the substance.

2. Conclusions and Perspectives

After this brief examination, it is clear how much “Protecting, conserving and handing down our past and present heritage” requires continuous study and research. Knowing the constituent materials of works of Art, the chemistry of the reactions involved in their degradation, and the material made available by plants, bacteria, and fungi are necessary actions for the development of new methodologies and innovative technologies that will allow the durability of the historic and artistic assets but above all, thanks to a creative operational “practice”, will allow this desirable and much-requested replacement/reduction of synthetic chemicals.

Acknowledgment

The SCN_00520 project supported by MIUR is acknowledged.

Heartfelt thanks to Doctors Sergio Sasso, Matteo Santacroce, Giacomo Napolitano and Nicoletta Sgarro for their contribution to the research.

References

T.D. Agostini-Costa - R.F. Vieira - H.R. Bizzo - D. Silveira - M.A. Gimenes, Secondary Metabolites. (2012), In: Sasikumar D, editor. Chromatography and its applications. London: InTech; https://doi.org/10.5772/35705.

M. Albini - L. Comensoli - L. Brambilla - E. Domon Beuret - W. Kooli - L. Mathys - P. Letardi - E. Joseph, Innovative biological approaches for metal conservation, Materials and Corrosion (2016), 67, No.2 www.matcorr.comwileyonlinelibrary.com©2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, doi:10.1002/maco.201408168

D. Aparaschivei - V. Vasilache - I. Sandu, A Study on Specific Archaeometric Characteristics of Garment Accesories found in the Ibida Site, Romania. International Journal of Conservation Science, (2012), 3(1): pp. 23-32.

V Argyropoulos - S. C. Boyatzis - M. Giannoulaki - E. Guilminot - A. Zacharopoulou, Organic Green Corrosion Inhibitors Derived from Natural and/or Biological Sources for Conservation of Metals Cultural Heritage, Microorganisms in the Deterioration and Preservation of Cultural Heritage, E. Joseph (ed.), (2021), pp 341–367.

J. Aromaa - M. Kekkonen, - M. Mousapour, - A. Jokilaakso, - M. Lundström, The Oxidation of Copper in Air at Temperatures up to 100 °C. *Corros. Mater. Degrad.*, (2021), *2*, 625-640.

A. Artesani - F. Di Turo - M. Zucchelli - A. Traviglia, (Recent Advances in Protective Coatings for Cultural Heritage–An Overview, Coatings, (2020), 10; 217; doi:10.3390/coatings10030217

J.G. Ávila-Hernández - M.L. Carrillo-Inungaray - R. De la Cruz Quiroz, et al. Beauveria bassiana secondary metabolites: a review inside their production systems, biosynthesis, and bioactivities. *Mex J Biotechnol. (*2020, 5:1–33. doi:10.29267/mxjb.2020.5.4.1.

E. Balliana - G. Ricci - C. Pesce - E. Zendri, Assessing the value of green conservation for cultural heritage: positive and critical aspects of already available. Methodologies International *Journal of Conservation Science*, (2016) Special Issue 1, pp. 185-202.

F.G. Bell, Durability of carbonate rock as building stone with comment on its preservation. Environmental geology (1993), 21: 187-200.

L.C. Braga - A.A.M. Leite - K.G.S. Xavier - J.A. Takahashi – M.P. Bemquerer – E. Chartone Souza - M.M.A. Nascimento, Synergic interaction between pomegranate extract and antibiotics against *Staphylococcus aureus.* Can J Microbiol., (2005), 51(7): pp. 541–7. https://doi.org/10.1139/w05-022.

L.B. Brostoff, Coating strategies for the protection of outdoor bronze art and ornamentation. Amsterdam: (2003), University of Amsterdam, Faculty of Sciences; https:*//dare.uva.nl/search?identifier=93a7bcf0-9545-4b70-a685-bf0a5110b0a7.*

D. Camuffo, Physical weathering of stones. The Science of the Total Environment (1995), 167: pp. 1-14.

E. Cano - D. Lafuente - D.M. Bastidas, Use of EIS for the evaluation of the protective properties of coatings for metallic cultural heritage: A review, J.Solid State Electrochem. (2010), 14; 381.

A.Berreghioua - A. Cheriti - N. Belboukhari, Flavonoids from the antibacterial extract of *Moricandia arvensis L.*growing in Algerian Sahara. Der Pharmacia Lettre, (2016), 8 (4): pp.45-49.

S. Chowński - Z. Adamski - P. Marciniak - G. Rosiński - E. Büyükgüzel - K. Büyükgüzel - P. Falabella - L. Scrano - E. Ventrella - F. Lelario - S.A.Bufo, A review of bioinsecticidal activity of Solanaceae alkaloids. Toxins.; (2016), 8(3): pp. 60, https://doi.org/10.3390/toxins8030060.

V. Costa - F. Urban, Lead and its alloys: metallurgy, deterioration and conservation, Reviews in Conservation, (2005), 6: 52.

F. De Leo, - A. Iero - G. Zammit - C. Urzì, Chemo-organotrophic bacteria isolated from biodeteriorated surfaces in cave and catacombs. International Journal of Speleology, (2012), 41: pp. 125-136.

A. Domenech-Carbo, Electrochemistry for conservation science, Journal of Solid-State Electrochemistry, (2010), 14(3): pp. 349-351.

A. Domenech-Carbo, Tracing, authenticating, and dating archaeological metal using the voltammetry of microparticles, Analytical Methods, (2011), 3: pp. 2181-2188.

V. Flexer - R. Grayburn - M. De Keersmaecker - A.A.M. Elbeshary - G. Dowsett Mark - A. Adriaens, A New Strategy for Corrosion Inhibition Coatings for Lead Heritage Metal Objects, Electrochimica Acta, (2015), Vol.179, 10.: pp. 441-451.

M. Fomina - S Hillier - J.M. Charnock - K. Melville - I. J. Alexander - G. M. Gadd, Role of oxalic acid over excretion in transformations of toxic metal minerals by Beauveria caledonica. Appl. Environ. Microbiol. (2005), 71, pp.371–381.

G. M. Gadd, Metals, minerals, and microbes: geomicrobiology and bioremediation., Microbiology (2010), 156; pp. 609–43. https://doi.org/10.1099/mic.0.037143-0

G. M. Gadd, Fungal production of citric and oxalic acid: importance in metal speciation, physiology,and biogeochemical processes. *Adv. Microb. Physiol. (*1999), 41: pp.48-92.

Gharieb, M. I., Ali, M. I., and El-Shoura, A. A. (2004). Transformation of copper oxychloride fungicide into copper oxalate by tolerant fungi and the effect of nitrogen source on tolerance. *Biodegradation* 15, 49.

F. D. Gonelimali - J. Lin - W. Miao - J. Xuan - F. Charles - M. Chen - S. R. Hatab, Antimicrobial Properties and Mechanism of Action of Some Plant Extracts Against Food Pathogens and Spoilage Microorganisms Front. Microbiol., Sec. Food Microbiology, (2018), Vol. 9, https://doi.org/10.3389/fmicb.2018.01639

LKMO Goni - AJM Mazumder, Green corrosion inhibitors. In: Singh A (ed) Corrosion inhibitors. Intech Open, London, (2019), pp. 13.

F. Green - C. A. Clausen, Copper tolerance of brown-rot fungi: time course of oxalic acid production. Int. Biodeterior. (2003), Biodegrad.51: pp. 145-149.

C. Hawks - M. McCann - K. Makos - L. Goldberg - H. DJr - D. Ertel - P. Silence (eds), Health and safety for museum professionals, 1st edn. (2010), Society for the Preservation of Natural History Collections, New York.

S. Bindschedler - M. Albini - L. Comensoli - W. Kooli - L. Mathys, Microorganisms for safeguarding cultural heritage. In: Dighton J, White JF, editors. The fungal community: its organization and role in the ecosystem. 4th ed.Boca Raton: CRC Press; (2017), pp. 509–18.

E. Joseph - S. Cario - A. Simon - M. Wörle - R. Mazzeo - P. Junier - D. Job, Protection of Metal Artifacts with the Formation of Metal–Oxalates Complexes by *Beauveria bassiana*. *Frontiers in Microbiology*, (2012), *2*(January), pp. 1–8.

V. Jurado - E. Porca - M. P. Pastrana - S. Cuezva - A. Fernandez-Cortes - C. Saiz-Jimenez, Microbiological study of bulls of indulgence of the 15^{th}-16^{th} centuries. Science of total Environment, (2010), 408: pp. 3711-3715.

V. Jurado - A. Z. Miller - C. Alias-Villegas - L. Laiz - C. Saiz-Jimenez, Rubrobacter bracarensis sp. nov., a novel member of the genus Rubrobacter isolated from a biodeteriorated monument. Syst Appl Microbiol. (2012), 35: pp. 306–309.

L. Laiz - G. Piñar - W. Lubitz - C. Saiz-Jimenez, Monitoring the colonization of monuments by bacteria: cultivation versus molecular methods. Environmental Microbiology (2003), 5: pp. 72-74.

P. Letardi, Laboratory and field test on patinas and protective coating systems for outdoor bronze monuments. In: Ashton J, Hallam D, editors. Metal 04 proceedings of the international conference on metals conservation. Canberra: National Museum of Australia, (2004), pp. 379–87 https://www.nma.gov.au/__data/assets/

P. Marciniak - A. Kolińska - M. Spochacz - S. Chowański - Z. Adamski - L. Scrano - P. Falabella - S. A. Bufo - G. Rosiński, Differentiated Effects of Secondary Metabolites from Solanaceae and Brassicaceae Plant Families on the Heartbeat of Tenebrio molitor Pupae. Toxins; (2019), 11:287., doi: 10.3390/toxins11050287.

R. Mazzeo - E. Joseph, Micro-destructive analytical investigation for conservation and restoration. In: Letardi P, Trentin I, Cutugno G, editors. Monumenti in bronzo all'aperto. Esperienze di conservazione a confronto. Florence: Nardini Editore; (2004), pp. 53–58.

A. Z. Miller - L. Laiz - A. Dionisio - M. F. Macedo - C. Saiz-Jimenez, Growth of phototrophic biofilms from limestone monuments under laboratory conditions. International Biodeterioration &Biodegradation, (2009), 63: pp. 860-867.

O. Mircea - I. Sandu - I. Sarghie - A. V. Sandu, The Identified Effects of Degradation in Archaeological Artefacts with Overlapped Metals Used in Authentication, International Journal of Conservation Science, (2010), 1: pp. 27-40.

A. Niklasson - L. G. Johansson - J. E. Svensson, Influence of acetic acid vapor on the atmospheric corrosion of lead, J. Electrochem. Soc. (2005), 152 B519.

S. Ordóñez - R. Fort - M.A. García del Cura, Pore size distribution and the durability of a porous limestone. Quarterly Journal of Engineering Geology, (1997), 30: pp. 221-230.

S. Papida - W. Murphy - E. May, Enhancement of physical weathering of building stones by microbial populations. International Biodeterioration and Biodegradation, (2000), 46: pp. 305-317.

J. L. Ramírez - M. A. Santana - I. Galindo-Castro - A. Gonzalez, The role of biotechnology in art preservation. Trends Biotechnol. (2005), 23, pp. 584-588.

L. Robbiola - J. M. Blengino - C. Fiaud, Morphology and mechanisms formation of natural patinas on archaeological Cu-Sn alloys, Corrosion Science, (1998), 40(12): pp. 2083 –2111.

L. Robbiola - R. Portier, A global approach to the authentication of ancient bronzes based on the characterization of the alloy – patina – environment system, Journal of Cultural Heritage, (2006), 7: pp. 1-12.

R. Reale - S. H. Plattner - G. Guida, M. P. Sammartino - G. Visco, *Ancient coins: cluster analysis applied to find a correlation between corrosion process and burial soil characteristics,* Chemistry Central Journal, (2012), 6:(2) s.9, (Conference on Multivariate Analysis and Chemometry to Cultural Heritage and Environment - CMA4CH, Taormina, Italy, September 26-29).

S. Sasso - A. Z. Miller - M.A. Rogerio-Candelera - B. Cubero - M. L. Coutinho - L. Scrano - S. A. Bufo, Potential of natural biocides for biocontrolling phototrophic colonization on limestone, (2016), 107: pp. 102-110

S. Sasso - L. Scrano - E. Ventrella - M. G. Bonomo - A. Crescenzi - G. Salzano - S. A. Bufo, Natural biocides to prevent the microbial growth on cultural heritage. *Proceeding of International Conference "Built Heritage 2013, Monitoring Conservation Management"* (2013), Milan, Italy 18-20 November.

S. Sasso - L. Scrano - M. G. Bonomo - G. Salzano - S. A. Bufo, Secondary metabolites: applications on cultural heritage. *Commun. Agric. Appl. Biol. Sci.* (2013), 78(2): pp.101-108.

J. A. Sayer - G. M. Gadd, Solubilization and transformation of insoluble inorganic metal compounds to insoluble metal oxalates by *Aspergillus niger*. *Mycol. Res.* (1997), 101, 653–661.

K. K. Schrager - J. Sobelman - A. Kingery-Schwartz, (2017), Not a known carcinogen. In: American Institute for Conservation 45th annual meeting on May 31st, 2017.

L. Scrano - R. Laviano - G. Salzano - S. A. De Franchi - J. Baranek - S. A. Bufo, (2020), Natural biocides and bio-calcite: innovative tools for cultural heritage, IOP Conference Series: Materials Science and Engineering, Volume 949, International Conference Florence Heritech: the Future of Heritage Science and Technologies, Online Edition doi: 10.1088/1757-899X/949/1/012096.

S. K. Sharma - A. Sharma, Green corrosion inhibitors: status in developing countries. In: Sharma SK (ed) Green corrosion chemistry and engineering: opportunities and challenges, 1st edn. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, (2012), pp 157–180.

S. Siegesmund - T. Weiss - A. Vollbrecht, Natural stone, weathering phenomena, conservation strategies and natural case studies: introduction. Geological Society, London, Special Publications, (2002), 205: pp.1-7.

M. Spochacz - S. Chowański - M. Szymczak-Cendlak - P. Marciniak - F. Lelario - R. Salvia - M. Nardiello - C. Scieuzo - L. Scrano - S. A. Bufo - Z. Adamski - P. Falabella, *Solanum nigrum* Extract and Solasonine Affected Hemolymph Metabolites and Ultrastructure of the Fat Body and the Midgut in *Galleria mellonella,* Toxins, (2021), 13(9): 617. doi: 10.3390/toxins13090617.

L. M. Suihko - L.H. Alakomi - A. A. Gorbushina - I. Fortune - S. M. Marquardt, Characterization of aerobic bacterial and fungal microbiota on surfaces of historic Scottish monuments. Syst. Appl. Microbiol. (2007), 30: pp. 494-508.

B. Szewczyk - L. Hoyos-Carvajal - M. Paluszek - I. Skrzecz - M. L. Souza, Baculoviruses e re-emerging biopesticides. Biotechnol. (2006), Adv. 24, 143-160.

Y. Unutulmazsoy - C. Cancellieri - M. Chiodi - S. Siol - L. Lin - L. P. H. Jeurgens, In situ oxidation studies of Cu thin films: Growth kinetics and oxide phase evolution. *J. Appl. Phys.*, (2020), *127*, 065101.

Y. Wan - X. Wang - H. Sun - Y. Li - K. Zhang - Y. Wu, Corrosion behavior of copper at elevated temperature. Int. J. Electrochem. Sci., (2012), 7, pp. 7902–7914.

M. E. Young - H. L. Alakomi - I. Fortune - A. A. Gorbushina - W. E. Krumbein - I. Maxwell - C. McCullagh - P. Robertson - M. Saarela - J. Valero - M. Vendrell, Development of a biocidal treatment regime to inhibit biological growths on cultural heritage: BIODAM. *Environ Geol.*, (2008), 56(3– 4):631–641. doi:10.1007/s00254-008-1455-1.

Paola Di Leo[1,2], Ester Maria Annunziata[2], Grazia Lubraco[3]

1. Institute of Metogologies for Environmental Analysis, National Research Council (IMAA – CNR), Tito Scalo (PZ), 85050, Italy; 2 Department of European and Mediterranean Cultures (DiCEM), University of Basilicata, Matera, Italy; 3 School of Specialization in Archaeological Heritage-Department of European and Mediterranean Cultures (SSBA-DiCEM), University of Basilicata, Matera, Italy

Micro X-Ray fluorescence imaging and chemical-mineralogical characterization of pigments in materials of artistic-cultural interest

Abstract

Among the most universal and best-known techniques for material analysis are optical and electron microscopy equipped with electron probe micro-analysis, X-ray diffractometry, X-ray fluorescence as well as Infra-Red and Raman spectroscopies. These techniques combine the possibility to magnify, visualize compositional variations, characterize crystallographic properties, and determine major and trace element composition of a variety of samples. Micro X-Ray fluorescence is a non-destructive technique and provides significant complementary information in the analytical process of complex sample evaluation. The present study is addressed to the archaeometric characterization of glaze and decoration of the Graffita ware from Moliterno Castle (Basilicata region, southern Italy) attested at the 14th and 15th centuries (with the Courtesy of the Superintendence of Basilicata). This is achieved through the acquisition of elemental distribution maps by micro X-Ray fluorescence using Bruker's M4 Tornado apparatus.

Keywords

Micro X-Ray fluorescence; glaze and pigments; Graffita ware.

Riassunto

Tra le tecniche più universali e conosciute per l'analisi dei materiali vi sono la microscopia ottica ed elettronica dotata di microanalisi, la diffrattometria di raggi X, la fluorescenza di raggi X e le spettroscopie a infrarossi e Raman. Queste tecniche combinano la possibilità di visualizzare le variazioni di composizione, caratterizzare le proprietà cristallografiche e determinare la composizione in elementi maggiori e in tracce di una varietà di campioni. La microfluorescenza di raggi X è una tecnica relativamente universale e fornisce informazioni complementari significative nel processo analitico di valutazione di campioni complessi. Il presente studio è rivolto alla caratterizzazione archeometrica dell'invetriatura e della decorazione della ceramica Graffita del Castello di Moliterno (Basilicata, Italia meridionale) attestata al XIV e XV secolo (su gentile concessione della Soprintendenza della Basilicata). Questo obiettivo è stato raggiunto attraverso l'acquisizione di mappe di distribuzione elementare in micro fluorescenza di raggi X, con l'apparecchiatura M4 Tornado della Bruker.

Parole chiave

Micro fluorescenza di raggi X; smalti e pigmenti; ceramica Graffita.

Introduction

The most universal and best-known techniques for material analysis are optical and electron microscopy (equipped with electron probe micro-analysis), X-ray diffractometry (XRD), X-ray fluorescence (XRF) as well as Infra-Red and Raman spectroscopies. These techniques combine the possibility to magnify and visualize compositional variations with the characterization of crystallographic properties and determination of major and trace element content (wt. % and ppm) for a variety of samples.

The X-Ray fluorescence technique - i.e. Energy Dispersive X-ray Fluorescence (EDXRF), Wavelength Dispersive X-ray Fluorescence (WDXRF), and micro X-Ray fluorescence (m-XRF) - is relatively universal and provides significant complementary information in the analytical process of complex sample evaluation. The conventional XRF techniques (EDXRF, WDXRF) are destructive and sample preparation is usually complicated and time-consuming. There is therefore a natural tendency to "optimize" the number of samples studied, which increases the chance of analytical misinterpretation due to non-representative sampling. In recent years much attention has been paid to develop analytical techniques able to avoid sample destruction (Tagle Berdan et al., 2019 and references therein).

In the followings we would like to focus on the more sophisticated technique µ-XRF (the non-destructive XRF tabletop technique) as a "first-line technique" and on its application in cultural heritage studies.

The µ-XRF: what is it and how it works

The obvious difference between conventional X-ray fluorescence analysis and µ-XRF is that µ-XRF uses a small spot to excite a predefined sample location. In conventional XRF, large sample areas of several millimeters are usually analyzed with the purpose of quantification. Therefore, in conventional XRF samples are prepared to optimize the conditions for quantification. This preparation involves homogenization (sample id destructed) often in combination with a reduction of the matrix effects by diluting the samples with low density materials. The sample preparation procedure ensures a standardized sample evaluation routine and high reproducibility of results. However, inhomogeneity of the sample can be an important aspect of the analytical question and most sample preparation is inherently destructive; the latter being an aspect in which spatially resolved XRF plays a key role.

The m-XRF technique is designed for the purpose of analyzing inhomogeneous samples. Quantification is still feasible, although requires caution and evaluation by the user. Use of a small defined beam - similar in principle to an electron beam but larger - allows indeed studies of the compositional variations of inhomogeneous samples. The small X-ray beam can be produced by using collimators or reflective optics such as mono- or polycapillary lenses. The small beam in the m-XRF, and relatively localized measurement position, can be used in single point mode or in scanning mode. In the latter, ideally, the full spectrum is saved for each measured location. This aspect (named position tagged spectroscopy) allows not only the creation of element distribution maps but also avoid the complex post-processing procedures.

The m-XRF instruments can be equipped with various types of X-ray sources and anode materials. Among these, the rhodium one is the most universal. This, on the one hand side, is due to its high melting point and good thermal conductivity, on the other hand, the Compton scattered characteristic lines of Rhodium overlap only with the elements Ru, Tc, Pd, and Cl. The overlap with Cl can be eliminated by using appropriate primary filters.

Primary filters are a common tool in μ-XRF where they are used to select the excitation spectrum or adapt it to the analytical task. Filters are made of one or more metal foils of known thickness. The filtering procedure – after having taken into consideration all these aspect – is very helpful to select specific energy ranges of the excitation spectrum. Indeed, this is chiefly eliminating the characteristic lines of the anode to reduce overlap with lines from the sample, e.g. Rh-L lines, W-L lines, or even Rh K lines in some instances. Primary filters also reduce the bremsstrahlung component resulting in a better peak-to-background ratio and can also reduce certain energy ranges of the spectrum that would be diffracted to produce artifact peaks on a sample of crystalline nature.

Fast analysis requires not only high excitation intensity but also detectors with high signal throughput which collect lots of counts and transfer them into the spectrum. There are several ways of increasing the detected signal. Using multiple detectors is one of these and allows processing signals in parallel and enable the user to "look" at samples from different directions. For the interpretation of element distribution images, the detector is considered the light source "illuminating" the sample and the beam (electron or X-ray) as the eye that is looking at the sample. By using multiple detectors, or even coaxial detectors, an easy understanding of the "shadow" regions on samples is achieved and the shadow-effect is minimized.

Micro X-ray fluorescence analysis is a non-destructive technique, and the sample can be analyzed without prior sample preparation. This makes the m-XRF instrument extremely accessible for fast initial assessment of samples by simply placing the sample in the chamber and analyzing it, and therefore a suitable instrument in cultural heritage studies, e.g painting, pottery, and other kind for artifacts whose size fits with the m-XRF chamber like papyrus.

The ideal sample for an electron-based excitation should be conductive. For μ-XRF analysis this is not required. *In principle*, any sample can be measured directly and without any sample preparation, including liquids, solids, or powders. However, some preparation or use of a specific sample holder might be required to achieve the best results. A measurement of the major and minor elements requires very little preparation and should always be possible. Only an intricate geometry might pose a problem in this case. For ideal quantitative analysis, the solid sample should be placed horizontal to the measurement plane, it should be infinitely thick (see later discussion), and homogenous within the analyzed volume.

Looking into the depths of matter

The spatial resolution of μ-XRF is, especially when compared to SEM-EDX, much coarser in all three dimensions, and it is extremely difficult to improve this. Sample depth information allows us to “see”, not only micrometers, but possibly even millimeters into the sample. Therefore, μ-XRF may open the 3rd dimension for compositional studies. This section shows some possibilities on how to analyze complex 3D samples.

One common way to utilize the penetrating character of X-rays is measuring the thickness of layered structures. While traveling through matter the radiation is attenuated, but also produces fluorescence on its path into the sample. This fluorescence intensity is then a measure for the thickness of the layer(s). Technically, it is the number of atoms in the beam path that are measured, and not thickness directly. This means that the density of the layered material is the most crucial parameter when converting the mass deposition (i.e., number of atoms per unit area) into the layer thickness. Unfortunately, density is not a well-known parameter, particularly for very thin layers and heavily depending on the layer deposition method. Nevertheless, it is more straight-forward to consider thickness when addressing some general guidelines for this type of application.

The applicability of X-ray layer thickness determination depends greatly on the sample system. For some layer structures the penetration depth may be the restricting parameter (for instance, Sn-rich solder layers), other samples are limited by the information depth of the produced fluorescence (most light-element layers). The measurement geometry also plays a large role. If both excitation and fluorescence radiation are detected (quasi-perpendicular), maximum measurable layer thicknesses are achieved. With lower angles the virtual layer thickness becomes larger, and hence the thickness range is more limited.

Information depth depends on the average atomic number of the sample and the fluorescence energy of the element in question. Excitation of an element’s fluorescence line is most efficient directly above the respective absorption edge. Higher energy photons can excite the atom, but the efficiency quickly diminishes. Thus, the depth from which the information is achieved can be reduced by changing the acceleration voltage within the X-ray tube (and thereby reducing the amounts of high-energy photons in the excitation spectrum). Therefore, the most effective possibility to reduce the depth from which the information is achieved is to evaluate a lower-energy fluorescence line of the same element. For example, using Pb-M instead of Pb-L reduces the depth from which the information is achieved from ~10 μm to approximately 1 μm in an Fe matrix. In an oil painting, which usually is a much less dense material than Fe, the effect is significantly more pronounced (Tagle Berdan et al., 2019 and references therein).

Figure 1. These element distribution images shown the distribution of lead in a painting. The first image shows the Pb-M lines at 2.4 keV and the second the Pb-La line at 10.54 keV. The difference in energies allows "display" of the element distribution at different depths. The L lines show the painting down to the grounding, including the damaged areas on the left side, and the M-lines show the topmost thin layers of Pb pigments present at the painting's surface (Tagle Berdan et al., 2019 and references therein).

This can be quite important aspect in artifact as well as in ancient ceramics, especially in medieval ceramics where the way of applying glaze and decorations is a crucial aspect in defining technology.

The high information depth requires consideration of the question of 'infinite thickness' in a wide variety of samples. Infinite thickness usually is a prerequisite for bulk quantification models. If the thickness of a sample could be increased continuously, the "infinite thickness" is the specific sample thickness from which on the fluorescence signal coming from the excited sample for any given element does not increase anymore (usually neglecting secondary excitation by fluorescence or scattered high-energy photons).

Understanding the medieval Graffita ware technology: an example of m-XRF potentials

In the following is showed how to use the m-XRF spectrometer M4Tornado (Bruker) to understand the technologies behind the production of Graffita ware from the Moliterno Castle (Basilicata) attested at the 14th and 15th centuries, with the Courtesy of the Superintendence of Basilicata (Annunziata, 2022; Annunziata et al., 2022).

Surface imaging (Mapping analyses) and spot analyses can be easily performed without any sample manipulation. Besides, simple sampling preparation as in Figure 2 allows analysis of ceramic body, including fabric evaluation, thus avoiding the use of the destructive OMA (Optical Microscopy Analysis) or at least confining this technique to only few diagnostic samples as a sort of "in situ" validation.

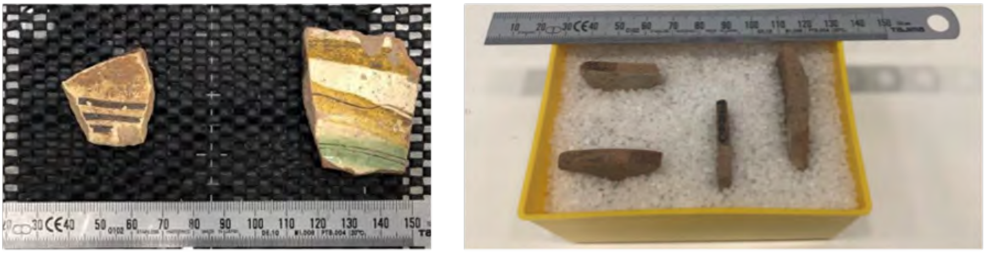


Figure 2. Internal portion of the M4 Tornado chamber. Large space allows to set samples in order to analyze multiple decorations in ware fragments as well as quantify composition of the cerami body as in thin sections.

When dealing with surface imaging, coupled with semi quantitative spot analysis, the analysis is sufficient to identify relevant sample areas. m-XRF spectroscopy, as shown in Figure 3, is able to identify the distribution of Sn in the Graffita ware fragments thus confirming the presence of tin (SnO_2) in the lead-glaze. Tin, as also suggested by XRD, is present in its crystalline form of cassiterite and appears to have been better preserved under the decoration, as it was mostly concentrated in the fragment portions (Annunziata, 2022; Annunziata et al, 2022). Comparing distribution of Sn-K_a lines with Sn-L_A lines allow some consideration of layer distribution of Sn. The first image shows the Sn-K_a lines at 25.27 keV and the second the Sn-L_A lines at 3.44-3.43 keV. The difference in energies allows "display" of the element distribution at different depths. The K lines show a distribution of Sn in the bright orange-colored areas and the L-lines show the topmost thin layers of Sn pigments in decoration present at the fragment surface.

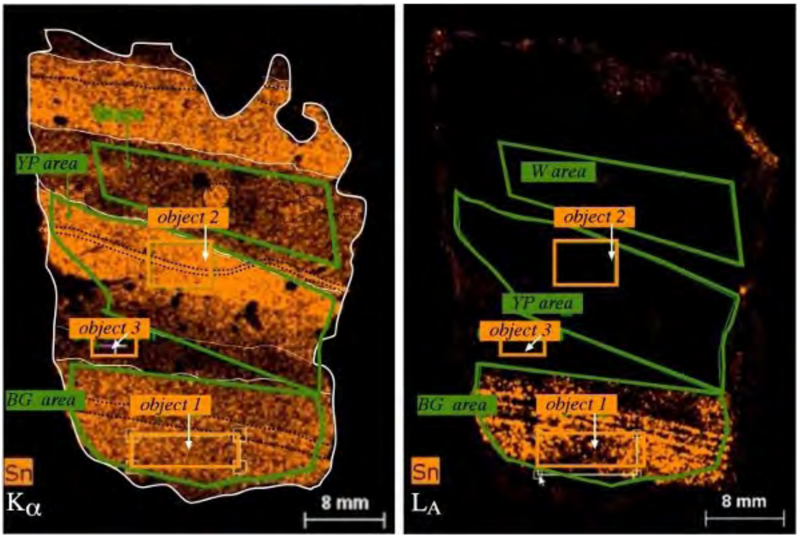


Figure 3. These element distribution images show the distribution of Sn in a Graffita ware. Objects represent the areas in which quantitative chemical compositin was achieved (Annunziata, 2022; Annunziata et al, 2022).W area = white-coloured area, YP area=Yellow Pale-colored area, and BG area= Bright Gree colored area as observed in the original ceramic fragment. Object 1, 2 and 3 depict the analized areas

Concluding remarks

The description and results presented here are intended to illustrate just some of the possibilities of µ-XRF not only as a pre-screening technique but also as a versatile analytical tool. The acceptance of this technique has increased in recent years due to its broad range of application and the required minimal sample preparation. Its wider distribution is illustrated in the increasing number of academic publications. Despite being a mature technique, a variety of developments are still taking place. Not only to apply it on an even wider variety of samples but also using it in completely new fields of application, such as automated mineral analysis. Further work is also done to take fundamental parameter quantification to the next level. The current and future improvements will most likely help this niche technique to become a standard for material analysis.

References

R. A. Tagle Berdan, F. Reinhardt, U. Waldschläger, T. Hill, T. Wolff, "*A deeper insight into materials: potentials and limitations of µ-XRF*", «Conference Proceedings_EMAS2019» (2019).

E. M. Annunziata, "*Archeologia e Archeometria della ceramica medievale: un ap-proccio multidisciplinare per la diagnostica dei manufatti cera-mici della Basilicata*", «Tesi di Dottorato di Ricerca, Università degli studi della Basilicata» (2022), pp 210.

E. M. Annunziata, G. Lubraco, B. Bravo, L. Medici, *Archaeometry of Basilicata Graffita ware: provenance and technology*, «Conference proceedings, IMEKO TC-4 International Conference on Metrology for Archaeology and Cultural Heritage, University of Calabria, Italy, October 19-21(2022).

Nicola Cardellicchio
Department of Science (DiS), University of Basilicata, Potenza
Francesco Cardellicchio
CNR, Institute of Methodologies for Environmental Analysis, Tito, Potenza

The impact of climate change on Cultural Heritage

ABSTRACT

Climate change, related to the gradual rise in temperature of the planet, is affecting cultural heritage sites. Consequently, there is a rapidly growing research sector that studies the effects of these changes, especially on artifacts exposed to the external environment, such as monuments, archaeological sites, historic buildings, etc. This work summarizes the environmental stressors that can modify the physical, chemical, and biological conditions, affecting the composition of the concerned materials. The main causes of degradation can have different origins: natural and man-made, the latter mainly represented by air pollution. However, there is no doubt that climate change modifies the water cycle, the acidity of the atmosphere, and the frequency and intensity of extreme events such as drought, floods, landslides, and sea levels. All these factors have inevitable repercussions on cultural heritage. Studying forecasting models is therefore essential not only for the assessment of the various impacts but above all for the adoption of mitigation and safeguarding policies.

KEYWORDS

Climate change, cultural heritage, stress factors.

RIASSUNTO

I cambiamenti climatici, relativi all'innalzamento graduale della temperatura del pianeta, stanno influenzando i siti del patrimonio culturale. Di conseguenza, c'è un settore di ricerca in rapida crescita che studia gli effetti di questi cambiamenti soprattutto sui manufatti esposti all'ambiente esterno, come monumenti, siti archeologici, edifici storici, etc. Questo lavoro sintetizza i fattori di stress ambientale che possono modificare le condizioni fisiche, chimiche e biologiche, che influenzano la composizione dei materiali interessati. Le principali cause di degrado possono avere differente origine: quella naturale e quella antropica, rappresentata quest'ultima principalmente dall'inquinamento atmosferico. È comunque indubbio che i cambiamenti climatici modificano il ciclo dell'acqua, l'acidità dell'atmosfera, la frequenza e l'intensità di eventi estremi come siccità, inondazioni, frane, livello del mare. Tutti questi fattori hanno inevitabili ricadute sul patrimonio culturale. È dunque indispensabile lo studio di modelli previsionali non solo per la valutazione dei diversi impatti, ma soprattutto per l'adozione di politiche di mitigazione e salvaguardia.

PAROLE CHIAVE

Cambiamento climatico, beni culturali, fattori di stress.

Introduction

Most of the entire historic-artistic heritage of the world is present in Italy. Currently no less than 57,000 "Cultural Assets" are registered on the national territory, of which 5,000 of an archaeological nature and over 50,000 of an architectural nature (Accardo et al., 2002, 2003). Italy, therefore, has a great responsibility for the conservation and enhancement of this immense heritage. Historical buildings, archaeological sites, and monuments are a reminder of the past, but in the present, they also represent a factor of socio-economic growth of the territory (Cassar, 2009; Phillips, 2015). Climate change, demonstrated by factors such as temperature increases, extreme events, intense rainfall and winds, and sea level rise, negatively affects the conservation of cultural heritage. In recent years, actions and research have therefore increased to understand the influence of environmental and climatic factors, especially on monuments and works of art exposed to the external environment. Climate change can affect the physical, chemical, and biological characteristics of structures and the composition of materials. One of the major factors of impact, especially in archaeological sites near the coast, is also represented by sea level rise, the intensity of storm surges, coastal erosion, flooding, and changes in river dynamics (Howard et al., 2008; Sabbioni et al., 2010; UNESCO, 2007). In this regard, governance for the protection of cultural heritage and a multidisciplinary approach with coordinated actions and the involvement of different actors at various institutional levels are urgently needed. The degradation depends on both natural and anthropic factors. The deterioration process is often progressive and irreversible; the timing of the impact depends on the type of material and the physical-chemical and biological agents involved. However, the degradation of materials is a complex phenomenon: the synergistic action of environmental and climatic factors leads to aesthetic and/or structural damage to the original material; these damages that can compromise the perception and use of the work itself and cause its loss of value. Important damages include surface recession due to thermal stress, blackening, alterations caused by freeze-thaw cycles, crystallization of salts, corrosion of metals, and biological growth. All these aspects are taken into consideration and discussed in this article.

Climatic factors and Cultural Heritage

The climatic factors that most influence the materials are temperature (daily temperature range), freeze and thaw cycles, thermal shocks, extreme rain events, relative humidity, wind, transport, deposition of sea spray, and air pollution. In particular, the Mediterranean regions are subject to high thermal stress (thermoclasticism), with damage amplified by wind erosion. Certainly, one of the factors that most of all influences the deterioration of stone materials, especially if porous, is the presence of water in the structures. This phenomenon triggers most of the physical (freeze and thaw, salt crystallization, beating action of rain) and chemical (solvent, hydrolyzing, and hydrating action of water) degradation mechanisms. Forecast models indicate that the chemical dissolution of carbonate stone materials is mainly due to the increase of the CO_2 concentration in the atmosphere and in precipitation with a consequent increase in the surface recession that in Italy can be estimated at around 30% (Sabbioni & Brimblecombe, 2010).

Physical factors

The degradation linked to physical factors is essentially due to sharp changes in temperature (thermoclastism), freeze-thaw phenomena (cryoclastism), crystallization of salts (haloclastism). These processes are found in very cold climates or in very hot and dry ones, where the fracturing of the rocks is due to sharp changes in temperature caused by insolation. Factors that directly influence the phenomena of physical deterioration are the mineralogical composition of the rock, its grain, and its texture (Brimblecombe, 2014). Physical deterioration also leads to an increase in the specific surface area available for chemical alteration which is always possible. The ingress of water into the structures favors the degradation of the material through corrosion mechanisms, biological activity, and sub-florescence due to the crystallization of salts (Curtis, 2016; Sabbioni et al., 2008; Sabbioni et al., 2010). A characteristic common to all stone materials, which strongly conditions their behavior over time, is undoubtedly the porous structure. It has been seen how the percentage of empty spaces with respect to the total volume can vary within very wide limits depending on the material and the process of genesis and how, with the same total porosity, structures with different distributions of pores can be obtained according to their diameter. In any case, the presence of empty spaces into which water and saline solutions can penetrate determines the possibility of important alteration phenomena occurring. The great affinity of water molecules for stone materials is due to the fact that weak electrostatic forces are exerted between the dipoles of the water and those present in the structures constituting the minerals. Water is therefore a "wetting" liquid and when it comes, for some reason, in contact with porous materials it is "sucked" into capillaries of the structure, with a force which, other factors being equal, is inversely proportional to the diameter of the capillaries themselves. Therefore, the system of intercommunicating capillaries can be considered as a continuous passageway, in which water penetrates very easily and within which it can move, depending on the external thermo-hygrometric conditions. If the temperature of the stone material drops to the freezing point of the water contained in its porous network, damage related to the formation of ice may occur. Most of the researchers who have studied the "freezing" in porous materials agree that the deterioration is linked to the phenomena of volume variations that accompany the transition from water to ice (Steiger et al., 2011). Thermoclasm is predicted to increase in the Mediterranean region with climate change (Camuffo, 2019; Sabbioni et al., 2008; Sabbioni et al., 2010), especially for the widely used Carrara marble (Bonazzaet al., 2009). Some actions in this regard have already been undertaken as, for example, the covering of archaeological sites: however, the exposure of these sites to solar radiation, wind, and rain leads to their considerable deterioration (Becherini et al., 2016).

Salt crystallization

Other causes of physical disintegration are linked to soluble salts which, as they crystallize, increase in volume and exert very high pressures inside porous rocks; these pressures can crush rocks that do not resist tensile stresses. A mechanism similar to the formation of ice crystals in the pores can be hypothesized to explain the effects produced by the crystallization of soluble salts. The water absorbed by a porous material is not pure, but it can contain organic and inorganic substances coming from the atmosphere, from the ground, or from the material itself. When the evaporation of the water (facilitated by the increase in temperature or by the decrease in the relative humidity of the air) increases the concentration of the saline substances present, these will tend to solidify, generally in the form of crystals. The crystals that form grow by exerting a crystallization pressure on the walls of the capillaries of the materials. The phenomenon of crystallization is often accompanied by that of hydration/dehydration to which volume variations are once again linked (Charola, 2000). The saline crystallization can manifest itself either in the form of efflorescence when it occurs on the evaporation surface and this coincides with the real external surface of the material from which the water evaporates or in the form of sub-florescence when the evaporation surface is located inside the material. The alteration caused by soluble salts causes alveolarization which manifests itself with the formation of often very deep alveoli. This alteration can be found above all in the case of stone materials with high porosity. Some salts can change their structure during their cycle of hydration and dehydration, for example, sodium sulfate (Rodriguez-Navarro et al., 2000; Brimblecombe & Grossi, 2007; Sabbioni et al., 2010; Camuffo, 2019) predicted an increase in crystallization events of soluble salts especially in central Europe, due to the expected decrease in relative humidity during the summer.

Air pollution and corrosion

In a warmer climate, an increase in metal corrosion processes and surface recession of carbonate stones such as marble is expected (Brimblecombe et al., 2011; Camuffo, 2019; Lefèvre, 2014; Sabbioni et al., 2008, 2010). Corrosion causes a deterioration of materials by the action of water and is influenced by acid rain in relation to the increase in atmospheric carbon dioxide. Corrosion of metals should be greater in coastal areas due to the salts contained in the marine aerosol.

Increasing CO_2 concentration also increases the karst recession of carbonate stones due to further acidification of precipitation (Bonazza et al., 2009 a).

The net loss of material (erosion) occurs above all in areas exposed to the washing away action of rain, to blackening, caused by the deposition of carbonaceous particles on the surface, and to physical stress caused by climatic and microclimatic factors (de la Fuente et al., 2013). For stone materials, one of the most widespread and applied mathematical damage functions is that of Lipfert (1989), in which the surface recession, proposed for any type of limestone, is estimated as a function of rainfall, the pH of the rain, the concentrations of SO_2 and nitric acid (HNO_3). The Lipfert function, valid for rainwater pH values between 5 and 6, overestimates the contribution of the karst effect and does not consider that of the atmospheric particulate which is present in significant concentrations in urban areas (Bonazza et al., 2009).

In its most recent formulation proposed by Kucera in the context of the European projectMulti-Assess (2007), the surface recession of stone materials (expressed in μm/year) was also estimated according to the concentrations of SO_2, HNO_3 and atmospheric particulate matter (PM10) (Kucera et al., 1993, 2007).

Sulfur dioxide (SO_2) and nitrogen oxides (NOx), react with water to produce sulfuric and nitric acid, increasing the acidity of the atmosphere (Haneef et al., 1992; Sabbioni et al., 2006) predicted an increase in carbonate rock recession, especially for the mountainous regions of Europe due to higher rainfall and a warmer and wetter climate.

The surfaces of buildings located in urban environments where there is a polluted atmosphere are destined to become covered with dark deposits which can take on different shapes and thicknesses. These deposits, which appear in the form of heterogeneous encrustations, are called "black crusts" (Figure 1). The main component of black crusts is gypsum present in the form of needle-like crystals (La Russa et al., 2013; Comite et al., 2020). The transformation of calcite into gypsum and the formation of new crystals cause tensions within the structure causing loosening and detachments of large limestone fragments. However, particles of various kinds can be incorporated in the gypsum such as atmospheric particulate matter, pollen, oxalates, bituminous and carbonaceous substances (responsible for the grey-black coloration), fragments of calcite (of the primary origin or derived from the dissolution of calcium carbonate ($CaCO_3$) and subsequent reprecipitation), quartz crystals and felspars (Ruffolo et al., 2015). In some cases, where bird droppings have been added to the black crust, calcium, and potassium phosphates have been identified. The black crusts can swell or produce exfoliations and flakes; over

Figure 1. Example of black crust formation.

time the crusts tend to thicken and harden more and more until they become less porous, thus accentuating the difference in mechanical and thermal behavior with the underlying stone. The role of the microclimate in the mechanism of genesis of the black crust is relevant: conditions of high relative humidity and frequent freezing temperatures are factors that increase the frequency of formation of these compact deposits.

Biological degradation

The term biodeterioration was defined by Hueck (1965) as "any undesirable change in the properties of a material, caused by the vital activity of living organisms". For a long time, the biological effects on materials were considered to direct consequences of physical and chemical degradation processes and immediate results of atmospheric pollution phenomena. Furthermore, it was believed that the phenomena of biodeterioration only modified the substrate from an aesthetic point of view, inducing the appearance of patinas and colored spots on the surface, following the release of biogenic pigments.

Recently, various analytical approaches have demonstrated the role played by microorganisms in deterioration phenomena, which, even in the early stages of exposure, are responsible for physical, chemical, and aesthetic modifications of the colonized surface (Urzì & Albertano, 2001). Microorganisms can use the surface as a support for growth, using mineral components or surface deposits as metabolites necessary for development. Architectural assets are to be understood as complex and heterogeneous environments; the heterogeneity is linked to the numerous interrelationships between the various biological populations and between these and the stone substrate.

However, the main agents of biodeterioration are autotrophic microorganisms. Heterotrophic microorganisms settle on the inert organic remains of autotrophs. Consequently, from the point of view of the settlement, they are considered secondary agents of biodeterioration. The environmental parameters which most influence the development and growth of the various biological groups are light, essential for photosynthetic organisms, oxygen, necessary for cellular respiration, carbon dioxide, necessary for the organication of carbon operated by autotrophs, water, essential to all organisms for carrying out the various metabolic functions. Some mineral salts are also needed, which can be supplied by the stony material and, for heterotrophic organisms, a source of organic carbon. The most widespread biodeteriogens on stone artifacts and for which it is easier to identify the harmful effect are undoubtedly microscopic algae. Often these are implanted on the surface of very porous materials, or in any case already deteriorated, and penetrate the micro-fractures or under fragments that are already partially detached. Lichens are also very widespread agents, at least in conditions of low air pollution, and very often they are easily recognizable, even by non-specialists, thanks to their characteristic macroscopic shapes and bright colors, yellow, white, and orange. There is no unanimity of opinion from scholars on the effects produced by lichens and there are even those who consider them protective of the surfaces on which they grow. In some cases, however, a corrosive action is ascertained, especially with regard to calcareous materials, produced by their acid metabolites.

The production of organic acids by organisms (particularly fungi) is a highly studied phenomenon that has profound implications for the conservation of stone materials. Oxalic acid in limestone rocks is responsible for the precipitation of calcium oxalate.The formation of calcium oxalate produces salts that are not very soluble but more soluble than calcium carbonate, which can be washed away, producing brown veils on the surface of the rocks.

Most naturally occurring oxalic acid salts (oxalates) are of biogenic origin. These are found within the biofilm on the rock surface, because ofthe interaction of the metabolic products of lithobiotic microbial communities (microscopic fungi, lichens, and bacteria) with rocks and minerals (Gadd et al., 2014; Kuz'Mina et al., 2019).

The role of chemosynthetic bacteria, especially those of the sulfur and nitrogen cycle, in stone alteration processes is still the subject of studies and insights. Similarly, it is not easy to evaluate the damage caused by fungi, actinomycetes, and heterotrophic bacteria, at least when there are no residues of an organic nature on the stone, such as, for example, protective agents applied in the past. If so, fungi may be an important cause of the damage (Ghany et al., 2019). In this context, it is important to pay attention to the assessment of the resistance of organic products used for the consolidation and protection of stone materials. This is a requirement that is generally not taken into consideration by those who carry out checks on the treatments. On the other hand, other characteristics being equal, the use of products not easily attacked by the various biodeteriogens could certainly provide a greater guarantee of the durability of the treatment.

Among the macroscopic organisms, ruderal plants and weeds often represent a serious problem for the conservation of archaeological structures, not only because with their development they can prevent or reduce their visibility, but also because the roots, penetrating the joints between the ashlars of stone and inside pre-existing fissures, they exert a harmful wedge action. In addition to the mechanical damage, chemical exchange mechanisms also come into play between the H^+ ions of the roots and the alkaline and alkaline earth cations of the minerals making up the stone which cause a slow transformation. Albeit at a less important quantitative level, the problem of weeds also concerns architectural structures that are not in a state of ruin, which still perform the function for which they were built. In fact, it is not uncommon to see tufts of grass or small shrubs sprouting luxuriantly on the roofs and in other inaccessible parts of churches and palaces, sometimes not devoid of their beauty, but certainly of little benefit to the monument.

Natural phenomena

Catastrophic phenomena in the natural environment resulting from climate change, such as floods, sea level rise, and landslides can have a great impact on cultural heritage. Flooding, for example, is one of the most important consequences of climate change.

The frequency and extent of flooding are expected to increase in Europe in the near future (Sabbioni et al., 2010) with losses of coastal areas.

One of the most alarming consequences of climate change is the rising sea levels, a phenomenon that proceeds at a rapid pace and which, in the absence of countermeasures, risks drowning 50 densely populated coastal cities in the span of half a century. By 2100, sea level rise is projected to be 0.3 - 1.1m in nearly all of the world's oceans related to rising atmospheric concentrations of greenhouse gases (IPCC 2019). Sea level rise can increase the severity of extreme ocean events, such as exceptionally high tides, storm surges, and unpredictable weather events, affecting both coastal and nearshore sites. In turn, tidal rivers can extend inland the effects of coastal flooding caused by both the short-term combination of surges, tides, and waves and long-term sea level rise. Sea level rise poses a significant threat to the cultural heritage located in coastal areas (Perez-Alvaro, 2016). Marzeion&Levermann (2014) estimated that 19% of this global heritage could be lost to flooding under a 3°C warming scenario. 42 of 49 World Heritage Sites on the Mediterranean coast have been identified as already at risk from coastal erosion (Figure 2).

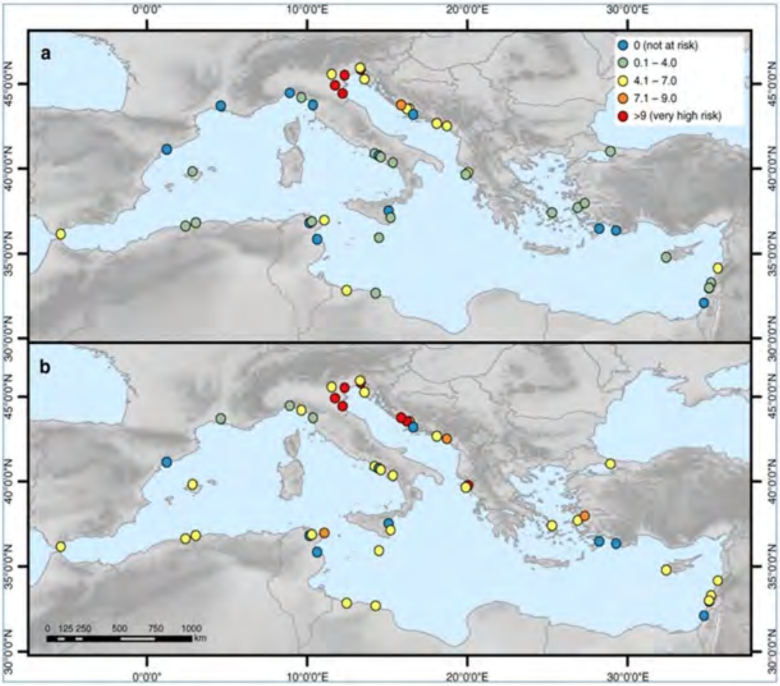


Figure 2. Flood risk index at World Heritage sites under current and future conditions: a in 2000 and b in 2100 under the high-rise sea level scenario (Reimann et al., 2018).

Changes in ocean properties such as temperature, salinity, and acidity are other important factor. Warmer sea surface temperatures could cause changes in water currents, oxygen levels, and salinity (Perez-Alvaro, 2016; Wright, 2016). Furthermore, greater absorption of atmospheric CO_2 by the oceans would lead to the acidification of the waters with an influence on the underwater heritage, in particular wrecks and submerged archaeological sites (Dunkley, 2013; 2015; Perez-Alvaro, 2016).

Coastal ocean waters experience natural pH fluctuations on a daily, seasonal, and interannual scale. Since the Industrial Revolution, the acidity of the ocean surface has increased by 30%, resulting in a decrease in pH. A further doubling or tripling of acidity could occur by 2100, as the oceans absorb more CO_2 released by human activities related to population growth and rising living standards. The direct effects of a decrease in sea pH affect a wide range of biological processes associated with the growth, reproduction, and survival of organisms that can both colonize and degrade underwater cultural heritage (Boyd, 2011).

Severe storms occur in mid-latitude regions, contributing to coastal erosion. Strong winds can create huge waves and storm surges that overflow natural and man-made coastal margins, causing flooding and saltwater incursions. In 2005, for example, much of a prehistoric settlement on the island of Baile Sear in Scotland's Outer Hebrides was destroyed when the sandy shoreline receded as much as 50m, causing structures to collapse, archaeological finds to be exposed and the dispersal of cultural material along the beach (Dawson, 2015). Strong winds can also cause coastal sands to shift: there is also an increased risk to maritime assets of pluvial flooding due to increased rainfall in both coastal and inland areas, especially during intense storms. This can be especially problematic if the river's water outlet is blocked at the coast by high sea level from surges or tides; the catastrophic Venice flood of 1966, for example, was in part caused by heavy inland rainfall throughout northeastern Italy combined with a high tide and strong winds (Trincardi et al., 2016).

Coastal erosion can destroy heritage sites gradually over decades or cause catastrophic losses during a single event (Dawson et al., 2020). Along the Libyan coast, for example, major settlements dating from the Greek, Roman, and Byzantine periods have been damaged by both types of erosion, including the ancient Greek city of Taucheira in Tocra, and the port of Apollonia in Cyrenaica, where the erosion of a protective natural reef has endangered the ancient port (Bennett, 2018). Similar coastal erosion is affecting archaeological sites in many other parts of the world, such as Cyprus (Andreou, 2018) and the pre-Columbian "mud city" of Chan Chan in Peru (Colosi et al., 2009; Pierdicca et al., 2016).

Conclusions

Climate change can increase the exposure of cultural heritage to stress factors due to gradual changes in climate, and the occurrence of extreme events. In reports published for a decade, UNESCO has mentioned the need to do more research on these impacts (UNESCO, 2007 a, b) which can be summarized as follows. Water is the main material degradation agent: an increase in rainfall, and humidity cycles, if combined with higher temperatures, can increase degradation processes such as corrosion, biological degradation, efflorescence and subflorescence due to salt crystallization.

An increase in the wind will affect cultural heritage, especially in the presence of sand, salt, and air pollutants. This can lead to surface abrasion, increased water penetration, structural damage, and collapse of structures.

A warmer temperature can lead to an increase in the number of freeze-thaw cycles with the onset of thermoclast phenomena. This can intensify the physical erosion of stone materials. An increase in temperature and relative humidity will increase biological degradation by creating conditions conducive to mold growth and insect activity.

Warming oceans can increase the risk of flooding and the disappearance of coastal areas. Desertification is also expected to increase in a hotter, drier climate, with the associated risk to cultural heritage.

To face these future challenges, it will therefore become increasingly important to monitor the state of health of an artistic asset. A long and expensive but indispensable procedure for acquiring the data necessary to establish whether the deterioration of a monument is attributable to structural changes triggered by the climate crisis, such as alterations in the water cycle and temperature, or whether it is due rather to pollution weather, a problem that has been struggled with for decades now.

References

Accardo G. – A. Altieri – C. Cacace – E. Giani – A. Giovagnoli, *Risk map: a project to aid decision-making in the protection, preservation and conservation of Italian cultural heritage*, Conservation Science, paper from the International Congress, Edinburgh, 22-24 May 2002, pp. 44-49.

Accardo G. – E. Giani – A. Giovagnoli, *The risk map of italian cultural heritage*, Journal of Architectural Conservation, 9 (2), (2003), pp. 41-57. https://doi.org/10.1080/13556207.2003.10785342

Andreou, G.M., *Monitoring the impact of coastal erosion on archaeological sites:* The *Cyprus Ancient Shoreline Project*, Antiquity. 92(361), (2018), e4. https://doi.org/10.15184/aqy.2018.1

Becherini, F. – J. Cassar – M. Galea – A. Bernardi, *Evaluation of the shelters over the prehistoric megalithic temples of Malta: Environmental considerations*. Environmental Earth Sciences, 75(14), (2016), 15 pp. https://doi.org/10.1007/s12665-016-5875-z

Bennett, P., *Notes from Libya,* Libyan Studies, 49, (2018). pp. 211–22. https://doi.org/10.1017/lis.2018.23

Bonazza A. – P. Messina – C. Sabbioni – C.M. Grossi – P. Brimblecombe, *Mapping the impact of climate change on surface recession of carbonate buildings in Europe,* Science of Total Environment, 407, (2009 a), pp. 2039 – 2050. https://doi.org/10.1016/j.scitotenv.2008.10.067

Bonazza, A. – C. Sabbioni – P. Messina – C. Guaraldi – P. De Nuntiis, *Climate change impact: Mapping thermal stress on Carrara marble in Europe*, Science of the Total Environment, 407(15), (2009 b), pp. 4506–4512. https://doi.org/10.1016/j.scitotenv.2009.04.008

Boyd, P.W., *Beyond ocean acidification*. Nature Geoscience, 4, (2011), pp. 273–74. https://doi.org/10.1038/ngeo1150

Brimblecombe P., *Refining climate change threats to heritage.* J. Inst. Conserv., 37, (2014), pp. 85–93. https://doi.org/10.1080/19455224.2014.916226

Brimblecombe, P. – C.M. Grossi – I. Harris, *Climate change critical to cultural heritage*. In H. Gökçekus, U. Türker, & J. W. LaMoreaux (Eds.), Survival and sustainability: environmental concerns in the 21st century, Springer, (2011), pp. 195–205.

Brimblecombe, P. – C.M. Grossi, *Damage to buildings from future climate and pollution*, APT Bulletin: The Journal of Preservation Technology, 38(2/3), (2007), pp. 13–18. Retrieved from www.jstor.org/stable/40004714

Camuffo D., *Microclimate for Cultural Heritage: Conservation, Restoration, and Maintenance of Indoor and Outdoor Monuments,* Book, Elsevier, Third Edition, (2019) 557 pp. https://www.sciencedirect.com/book/9780444641069/microclimate-for-cultural-heritage

Cassar M. – R. Pender, *The impact of climate change on cultural heritage: evidence and response,* ICOM Committee for Conservation, 14th Triennial Meeting, 12-16 September 2005, The Hague, James & James, pp. 610–616.

Charola A.E., *Salts in the Deterioration of Porous Materials: An Overview*, Journal of the American Institute for Conservation, 39(3), (2000), pp. 327-343. https://doi.org/10.1179/019713600806113176

Colosi F. - G. Fangi - R. Gabrielli - R. Orazi - A. Angelini - C.A. Bozz, *Planning the archaeological park of Chan Chan (Peru) by means of satellite images, GIS and photogrammetry,* Journal of Cultural Heritage, 10, (2009), pp. 27–34. https://doi.org/10.1016/j.culher.2009.08.002

Comite V. - J.S. Pozo-Antonio – C. Cardell – L. Randazzo – M.F. La Russa – P. Fermo, *A multi-analytical approach for the characterization of black crusts on the facade of an historical cathedral*, Microchemical Journal, 158, (2020), 105121. https://doi.org/10.1016/j.microc.2020.105121

Curtis, R., *Water management for traditional buildings: Adaptation for a changing climate,* APT Bulletin: The Journal of Preservation Technology, 47(1), (2016), pp. 8–14. Retrieved from www.jstor.org/stable/43799258

Dawson T. – J. Hambly – A. Kelley – W. Lees – S. Miller, *Coastal heritage, global climate change, public engagement, and citizen science,* Proceedings of the National Academy of Sciences of the USA 117: pp. 8280–86. https://doi.org/10.1073/pnas.1912246117

Dawson T., *Eroding archaeology at the coast: how a global problem is being managed in Scotland, with examples from the Western Isles,* Journal of the North Atlantic, 9, (2015), pp. 83–98. https://doi.org/10.3721/037.002.sp905

de la Fuente D. – J.M. Vega – F. Viejo – I. Díaz – M. Morcillo, *Mapping air pollution effects on atmospheric degradation of cultural heritage*, Journal of Cultural Heritage, 14, (2013), pp. 138–145. https://doi.org/ 10.1016/j.culher.2012.05.002

Dunkley M., *Climate is what we expect, weather is what we get: Managing the potential effects of climate change on underwater cultural heritage*. In W. Willems & H. van Shaik (Eds.), Water and heritage: Material, conceptual, and spiritual connections, Sidestone Press (2015), pp. 217–230).

Dunkley M., *The potential effects of oceanic climate change on the management of underwater archaeology,* The Archaeologist, 89, (2013). pp. 60–62.

Gadd G. M. – J. Bahri-Esfahani – Q. Li – Y.J. Rhee – Z. Wei – M. Fomina – X. Liang, *Oxalate production by fungi: significance in geomycology, biodeterioration and bioremediation*, Fungal Biology Reviews, 28(2-3), (2014), 36-55. https://doi.org/10.1016/j.fbr.2014.05.001

Ghany T.M.A. – A.M. Omar – F.M. Elwkeel – M.A. Al Abboud – M.M. Alawlaqi, *Fungal deterioration of limestone false-door monument,* Heliyon, 5 (10), (2019) e02673. https://doi.org/10.1016/j.heliyon.2019.e02673

Haneef, S. J. – J.B. Johnson – C. Dickinson – G.E. Thompson – G.C. Wood, *Effect of dry deposition of NOx and SO2 gaseous pollutants on the degradation of calcareous building stones*, Atmospheric Environment, Part A., General Topics, 26(16), (1992), pp. 2963–2974. https://doi.org/10.1016/0960-1686(92)90288-v

Howard, A. J. – K. Challis – J. Holden – M. Kincey – D.G. Passmore, *The impact of climate change on archaeological resources in Britain: A catchment scale assessment,* Climatic Change, 91(3–4), (2008), pp. 405–422. https://doi.org/10.1007/s10584-008-9426-9

Hueck H.J., *The biodeterioration of materials as a part of Hylobiology,* Mater. Org., 1, (1965), pp. 5-34. http://resolver.tudelft.nl/uuid:cd2e06b7-2a61-4685-96b9-08a490c6e2c0

IPCC, *Special report on the ocean and cryosphere in a changing climate*. Cambridge University Press (2019). https://www.ipcc.ch/srocc

Kucera V. – J. Henriksen – D. Knotkova – C. Sjöström, *Model for calculations of corrosion costs caused by air pollution and its applications in three cities. Progress in the understanding and prevention of corrosion,* Papers presented at the 10th European Corrosion Congress, Barcelona, Vol. 1, (1993), pp. 24-32.

Kucera V. – J. Tidblad – K. Kreislova – D. Knotkova – M. Faller – D. Reiss – R. Snethlage – T. Yates – J. Henriksen – M. Schreiner - M. Melcher – M. Ferm – R-A. Lefèvre – J. Kobus, *UN/ECE ICP materials dose-response functions for the multi-pollutant situation,* Water, Air, and Soil Pollution: Focus, 7(1-3), (2007), pp. 249-258. https://doi.org/10.1007/s11267-006-9080-z

Kuz'Mina M. A. – A.V. Rusakov – O.V. Frank-Kamenetskaya – D.T. Vlasov, *The influence of inorganic and organic components of biofilms with microscopic fungi on the phase composition and morphology of crystallizing calcium oxalates*, Crystallography Reports, 64(1), (2019), p. 161-167. https://doi.org/10.1134/S1063774519010176

La Russa M.F. – C.M. Belfiore – V. Comite – D. Barca – A. Bonazza – S.A. Ruffolo –G.M. Crisci – A. Pezzino, *Geochemical study of black crusts as a diagnostic tool in cultural heritage*, Applied Physics A, 113, (2013), pp. 151–1162. https://doi.org/10.1007/s00339-013-7912-z-

Lefèvre, R.A., *The impact of climate change on slow degradation of monuments in contrast to extreme events*. In S. von Schorlemer& S. Maus (Eds.), Climate change as a threat to peace, Peter Lang AG, (2014), pp. 83–100.

Lipfert F.W., *Atmospheric damage to calcareous stones: comparison and reconciliation of recent experimental findings*, Atmos. Environ., 23, (1989), 415–429. https://doi.org/10.1016/0004-6981(89)90587-8

Marzeion, B. – A. Levermann, *Loss of cultural world heritage and currently inhabited places to sea-level rise,* Environmental Research Letters, 9(3), (2014), 034001. https://doi.org/10.1088/1748-9326/9/3/034001

MULTI-ASSESS Project, *Model for multi-pollutant impact and assessment of threshold levels for cultural heritage*, Deliverable 02, Final Report (2007). http://www.corr-institute.se/ MULTI-ASSESS.

Perez-Alvaro, E., *Climate change and underwater cultural heritage: Impacts and challenges,*Journal of Cultural Heritage, 21, (2016), pp. 842–848.https://doi.org/10.1016/j.culher.2016.03.006

Phillips H., *The capacity to adapt to climate change at heritage sites—The development of a conceptual framework*. Environmental Science & Policy, 47, (2015), pp. 118–125. https://doi.org/10.1016/j.envsci.2014.11.003

Pierdicca R. – E. Frontoni – E.S. Malinverni – F. Colosi – R. Orazi, *Virtual reconstruction of archaeological heritage using a combination of photogrammetric techniques: Huaca Arco Iris, Chan Chan, Peru,* Digital Applications in Archaeology and Cultural Heritage, 3, (2016), pp. 80–90. https://doi.org/10.1016/j.daach.2016.06.002

Reimann L.,- A.T. Vafeidis – S. Brown – J. Hinkel – R.S.J. Tol, *Mediterranean UNESCO World Heritage at risk from coastal flooding and erosion due to sea-level rise*, Nature Communications, 9, (2018), 4161. https://doi.org/10.1038/s41467-018-06645-9

Rodriguez-Navarro, C. – E. Doehne – E. Sebastian, *How does sodium sulfate crystallize? Implications for the decay and testing of building materials,* Cement and Concrete Research, 30(10), (2000), pp. 1527–1534. https://doi.org/10.1016/s0008-8846(00)00381-1

Ruffolo S.A. – V. Comite – M.F. La Russa – C.M. Belfiore –D. Barca – A. Bonazza – G.M. Crisci – A. Pezzino – C. Sabbioni, *An analysis of the black crusts from the Seville Cathedral: A challenge to deepen the understanding of the relationships among microstructure, microchemical features and pollution sources,* Science of the Total Environment, 502, (2015), pp. 157–166. http://dx.doi.org/10.1016/j.scitotenv.2014.09.023

Sabbioni, C. – M. Cassar – P. Brimblecombe – R.A. Lefevre*, Vulnerability of cultural heritage to climate change*. Retrieved from Strasbourg: 20 November (2008), 24 pp. https://www.coe.int/t/dg4/majorhazards/activites/2009/Ravello15-16may09/Ravello_APCAT2008_44_Sabbioni-Jan09_EN.pdf

Sabbioni, C. – P. Brimblecombe – A. Bonazza – C.M. Grossi – I. Harris – P. Messina, *Mapping climate change and cultural heritage,* In: M., D. & M., C. (eds.). Safeguarding Cultural Heritage. Understanding & Viability for the Enlarged Europe., (2006) Prague, Institute of Theoretical and Applied Mechanics of the Academy of Sciences of the Czech Republic, pp. 119–124.

Sabbioni, C. – P. Brimblecombe – M. Cassar, *The atlas of climate change impact on European cultural heritage. Scientific analysis and management strategies*. Anthem Press, (2010). https://data.europa.eu/doi/10.2777/11959

Steiger M. – A.E. Charola – K. Sterflinger, *Weathering and Deterioration in Stone in Architecture*, Springer ed., (2011) pp. 227-316. https://doi.org/10.1007/978-3-642-14475-2_4

Trincardi F. – A. Barbanti – M. Bastianini – L. Cavaleri – J. Chiggiato – A. Papa – A. Pomaro –M. Sclavo – L. Tosi – G. Umgiesser, *The 1966 flooding of Venice: what time taught us for the future*, Oceanography, 29 (2016), pp. 178–86. https://doi.org/10.5670/oceanog.2016.87

UNESCO World Heritage Centre, *Climate change and world heritage. Report on predicting and managing the impacts of climate change on World Heritage and Strategy to assist States Parties to implement appropriate management responses,* Paris, France, World Heritage Reports 22, (2007a), 55 pp.

UNESCO World Heritage Centre, Policy document on the impacts of climate change on world heritage properties. Document WHC-07/16.GA/10 adopted by the 16th general assembly of states parties to the world heritage convention (2007b). http://whc.unesco.org/en/CC-policy-document

Urzì C. – P. Albertano, *Studying phototrophic and heterotrophic microbial communities on stone monuments*, in Doyle R.J (Eds.). Method Enzimol., 336, (2001), pp. 340-355.

Wright J., *Maritime archaeology and climate change: An invitation*, Journal of Maritime Archaeology, 11(3), (2016), 255–270. https://doi.org/10.1007/s11457-016-9164-5

Francesco Cardellicchio
CNR, Institute of Methodologies for Environmental Analysis, Tito, PZ
Fausto Langerame
Department of Science (DiS), University of Basilicata, Potenza
Anna Maria Salvi
Department of Science (DiS), University of Basilicata, Potenza

Use of the XPS technique for cultural heritage diagnostics

Abstract

In recent decades, the historic-artistic heritage has undergone greater degradation than in the past, in relation to the synergistic action of air pollution, climate change, and biological contamination. In addition to reducing pollution levels, the conservation of cultural heritage also requires the development of increasingly innovative, effective, long-lasting, and inexpensive research and protection strategies. As part of the MIUR project "Smart Cities, SCN_00520" research was launched on the state of conservation of San Pietro Barisano, one of the most important rupestrian churches in the 'Sassi' district of Matera. Since the church was excavated in the calcarenite rock, the research was mainly directed to an accurate diagnosis of the wall and masonry structures, based on a multi-technique and interdisciplinary approach, to respond to the ultimate objective of planning optimal and environmentally friendly restoration interventions. To that aim, XPS, the surface-specific technique, proved to be useful both for the possibility of analyzing small quantities of powdered samples, appropriately taken from degraded surfaces, and for the fastness of analysis which does not involve particular treatment of the collected sample, offering cognitive support for comparative analyzes with other techniques. In this study some examples of the diagnostic use of XPS are provided, describing the whole adopted procedure from sampling to spectra acquisition and data elaboration through a reliable curve-fitting programme. Three samples, collected from different colored areas of an internal wall of the church, were compared to identify their composition and eventually discriminate the chemical compounds in relation to the different types of degradation usually well evident. The results are discussed in the light of literature data and the XPS online database.

Keywords

San Pietro Barisano church, walls deterioration, XPS investigations, diagnostics/restoration.

Riassunto

Negli ultimi decenni il patrimonio storico-artistico ha subito un degrado maggiore rispetto al passato, in relazione all'azione sinergica di inquinamento atmosferico, cambiamenti climatici e contaminazione biologica. Oltre a ridurre i livelli di inquinamento, la conservazione del patrimonio culturale richiede anche lo sviluppo di ricerche e strategie di protezione sempre più innovative, efficaci, durature e poco costose. Nell'ambito del progetto MIUR "Smart Cities, SCN_00520" è stata avviata una ricerca sullo stato di conservazione di San Pietro Barisano, una delle più importanti chiese rupestri nel distretto dei 'Sassi' di Matera. Poiché la chiesa è stata scavata nella roccia calcarenitica, la ricerca è stata principalmente indirizzata ad un'accurata diagnosi delle pareti e strutture murarie, basata su un approccio multitecnico e interdisciplinare, per rispondere all'obiettivo ultimo di progettare interventi di restauro ottimali e rispettosi dell'ambiente. A tale scopo la tecnica XPS, specificatamente di superficie, si è rivelata utile sia per la possibilità di analizzare piccole quantità di campioni in polvere, opportunamente prelevati da superfici degradate, sia per la solidità dell'analisi che non comporta particolari trattamenti del campione prelevato, offrendo supporto conoscitivo per analisi comparative con altre tecniche. In questo studio vengono forniti alcuni esempi sull'uso diagnostico dell'XPS, descrivendo l'intera procedura adottata dal campionamento all'acquisizione degli spettri e alla loro elaborazione mediante un affidabile programma di curve-fitting. Tre campioni, prelevati da zone di diverso colore di una parete interna della chiesa, sono stati confrontati per individuarne la composizione ed eventualmente discriminare i composti chimici in relazione ai diversi tipi di degrado visivamente ben evidenti. I risultati sono discussi alla luce dei dati della letteratura e del database XPS.

PAROLE CHIAVE
Chiesa di San Pietro Barisano, degrado delle superfici, indagini XPS, diagnostica/restauro.

Introduction

The deterioration of stone materials is a complex phenomenon, often attributable not only to air pollution but also to the climatic conditions to which cultural heritage is subjected. The synergistic action of environmental and climatic factors often leads to aesthetic and structural damage to the original material, with a relative loss of its value. Knowledge of the processes that can affect the deterioration of materials is particularly important, especially for the choice of structural restoration interventions (Tzanis et al., 2009).

The degradation is due to physical, chemical, and biological phenomena. Among the various forms of degradation, the physical one is linked to sudden changes in temperature (thermoclasm), freeze-thaw phenomena (cryoclasm) (Steiger et al., 2011), and crystallization of salts (haloclasm). Factors that directly influence the processes of physical deterioration are the mineralogical composition of the rock, its grain, and its texture (Brimblecombe, 2014). Many causes of the disintegration of materials are linked to water and soluble salts which, by crystallizing, increase in volume and exert very high pressures inside porous rocks. Moreover, the phenomenon of crystallization is often accompanied by that of hydration/dehydration to which volume variations are once again linked (Charola, 2000).

A characteristic common to all stone materials, which strongly conditions their behavior over time, is undoubtedly the porous structure characteristic of Matera limestone. The water absorbed by a porous material can contain organic and inorganic substances coming from the atmosphere, from the ground, or from the material itself. When the evaporation of the water (facilitated by the increase in temperature or by the decrease in the relative humidity of the air) increases the concentration of the saline substances present, these tend to solidify, generally in the form of crystals which grow by exerting pressure on the rock walls.

Salt crystallization can manifest itself either in the form of efflorescence when it occurs on the evaporation surface or in the form of sub-florescence, when the evaporation surface, and consequently the crystallization zone, are located inside the material.

The morphology of the alteration caused by soluble salts can be very varied, depending on the conditions in which crystallization takes place, and on the structural characteristics of the stone material. In particular, pitting, which manifests itself with the formation of often very deep pits, is a form of alteration that disrupts materials, especially in the case of highly porous stones. According to Pauly et al. (2011), this particular alteration occurs when there is a combination of the following factors: high porosity, high content of very soluble and hygroscopic salts, and strong turbulence of the air in contact with the stone surface.

The set of variations in air temperature, relative humidity, material surface temperature, incident solar radiation, and wind intensity, therefore, define the factors and the microclimate to which a material is subjected (Bonazza et al., 2009). Water also favors chemical reactions which not only lead to the deterioration of the material but also to the incorporation of suspended particles in the surface layers. The high relative humidity of the air also favors the growth of biological activity on stone surfaces, resulting in damage to the surfaces themselves. All the monumental artistic heritage is continuously subject to biological attack by various forms of living organisms: bacteria, fungi, algae, lichens, mosses, vascular plants, and, last but not least, birdlife (Bartoli et al., 2014; Coutinho et al., 2015; Urzì et al., 2001). Both fungi and lichens, for example, adhere to carbonate substrates by means of root systems called hyphae. The combined action of the penetration of the hyphae into the material and the release of acid substances (e.g. oxalic acid) and/or metal chelators (e.g. Ca, Mg) produces chemical/mechanical stress. The effect on the stone (high alveolization) is only visible when the biological colony is already extinct.

Recently, in the context of the multidisciplinary and multi-technique research approaches of the Smart Cities National project, all the possible factors affecting the degradation were considered in the study of the Church of San Pietro Barisano, one of the most important rock churches of the "Sassi of Matera" (AIES I & II, 2021). In particular, the characterization of the patina covering the hypogeum walls of 'San Pietro Barisano' by surface techniques XPS, SEM and biological assays, has given an insight into the role played by the colonizing microorganisms, before and after treatment with glycoalkaloids, as a natural biocide (Cardellicchio et al., 2023) and, more in general, on the chemical and microbial correlation of degraded surfaces.

As part of the SCN_00520 project, a wide variety of samples taken from wall surfaces inside the church was collected for analysis with XPS and other techniques in order to classify the various types of degradation as a function of the internal location and to offer the first important cognitive support for designing and planning the recovery interventions, shared within the SCN scientific community. Examples of the XPS ability to discern surface composition at the nanometres scale are given in this work by considering three samples of the large collection, nearly located inside the church but showing different degradation routes.

Materials and methods

Study site

The Church of San Pietro Barisano is a perfect example of the typical architectural structure of the Sassi of Matera (Figure 1). The church has a tuff facade with the interior almost completely excavated, dating back to the year thousand, and known in the past by the name of San Pietro in Veteribus. The interior consists of three naves divided by imposing carved pillars that support round arches and presents six atars also made from tuff. The high altar is from the eighteenth century and is in gilded wood. In the right aisle, a small opening near the first altar dedicated to St. Joseph leads into a room dating back to the fifteenth-century modifications which was walled up in the 18th century and used as an ossuary.

Figure 1. The facade and two altars inside the church of San Pietro Barisano (https://it.wikipedia.org/).

The church of San Pietro Barisano shows evident phenomena of degradation both on the outside and, above all, on the inside, of the calcarenite from which the structure is composed. By way of example, on the two altars of Figure 1 and in the surroundings, chromatic alterations of the stone surfaces, the presence of patinas, efflorescence, alveolizations, and detachments of some portions of the walls were observed.

Sample collection and XPS analysis

Figure 2 shows the layout of the main architectural elements of the church and the degraded areas where the sampling was performed are reported circled in red. The powder samples were delicately taken from the walls with a steel spatula, removing only the surface patina or other degradation products, trying to preserve deeper layers not to damage the underneath structure.

Figure 2. Plan of the church of San Pietro Barisano: the sampling areas are circled in red.

The systematic collection of gently scraped powders (homogenized for XPS analysis) was aimed at determining eventual differences in chemical composition as a function of internal location and specific environment (Cardellicchio, 2022). Of the large collection (whose multivariate data processing is in progress), in this contribution, we report on the comparison of three samples numbered #1, #3, and #5 taken along the degraded wall located on the right side of the main altar (point 5 of the entrance plan), horizontally, corresponding to close but differently colored surface zones as clearly evidenced in Figure 3.

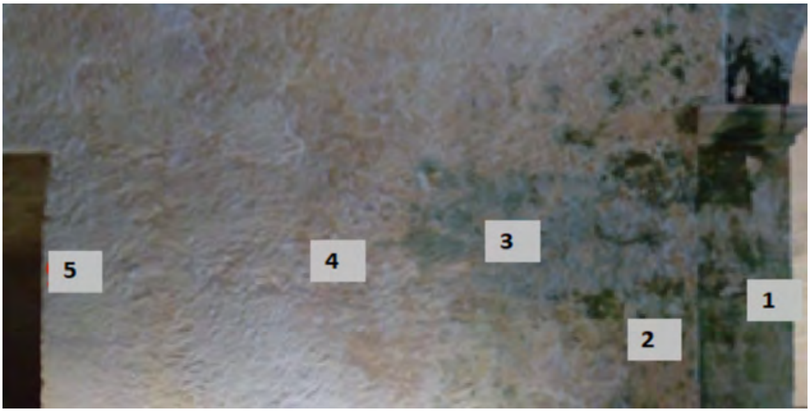


Figure 3. Sampling points on a degraded wall with surface patinas of different colors.

Samples gently scraped off from surfaces were stored for XPS analysis in Eppendorf tubes. The collected powders were firstly homogenized in an agate mortar and then pressed onto a double-sided copper tape, properly fixed on a steel sample holder, to be safely introduced in the analysis chamber of the spectrometer. XPS spectra were acquired with a SPECS Phoibos 100- MCD5 spectrometer operating at 10 kV and 10 mA, in medium area (diameter = 2 mm) mode, using a MgKα (1253.6 eV) and AlKα (1486.6 eV) radiations. The use of the double anode (Al/Mg) helps to distinguish XPS signals, varying in kinetic energy (KE) with the source employed, from the X-ray-induced Auger signals, dependent only on atomic relaxation following photoemission and therefore recognizable at the same KE (eV) with both sources (Briggs & Seah, 1990; Briggs & Grant, 2003).

The pressure in the analysis chamber was less than 10^{-9}mbar during acquisition. Wide spectra were acquired in FAT (Fixed Analyser Transmission) or FRR (Fixed Retarding Ratio) modes with channel widths of 1.0 eV. High-resolution spectra were acquired in FAT mode, with a constant pass energy of 9 eV and channel widths of 0.1 eV, and were "curve-fitted" using the Googly program, which allows evaluating intrinsic and extrinsic features of XPS spectra (Castle & Salvi, 2001; Castle et al., 2000).

Peak areas and positions (Binding Energies, BE) as derived by "curve fitting" were, respectively, normalized using proper sensitivity factors and referenced to the C1s aliphatic carbon, as internal standard, set at 285.0 eV (Briggs & Seah, 1990; Briggs & Grant, 2003). The chemical groups assignments were derived from the laboratory analysis of standard compounds, and from the NIST X-ray Photoelectron Spectroscopy Database (NIST, 2012) and related literature data cited in the text. In addition to the corrected BE values, the distance between the main Auger and XPS signals of the given element, tabulated as combined Auger parameter (α'), is very important for confirming chemical assignments given its independence from the energy reference level and surface charging of non conductor samples (Briggs & Seah, 1990; Briggs & Grant, 2003).

The normalized peak areas, were then converted into percent atomic composition (At%) and used for semi-quantitative analyses, here reported in the form of pie charts, for each analyzed sample.

Results and discussion

Figure 4 shows the 'wide' spectra recorded in the FAT mode for samples #1,3 and 5 of Figure 3, selected for comparative compositional analysis. The photoelectron and Auger signals were all identified by comparison with the tabulated values of KE and the main regions labeled following the ascending order in the energy scale: Mg1s, Na1s, O1s, N1s, Ca2p, C1s, Cl2p, S2p, Si2p, were then acquired at higher resolution, as detailed regions.

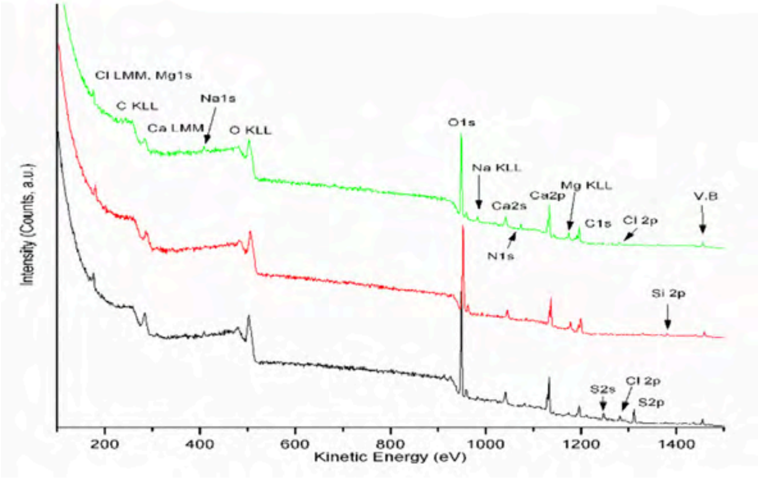


Figure 4. Wide spectra of samples #1(black) #3 (red) and #5 (green) recorded in FAT mode.

The detailed regions better characterising sample #1, are reported in Figure 5, as an example of the curve-fitting procedure adopted for spectra elaboration. Of these, the main carbon region, deriving from the 1s orbital, was first resolved by curve fitting into five peak components (Figure 5, left) whose assignment was also useful to identify the aliphatic/aromatic C1s signal whose binding energies set at 285.0 eV was taken as the internal standard to corrected all binding energies (BE corrected) and define the related attributions, as shown in Table 1.

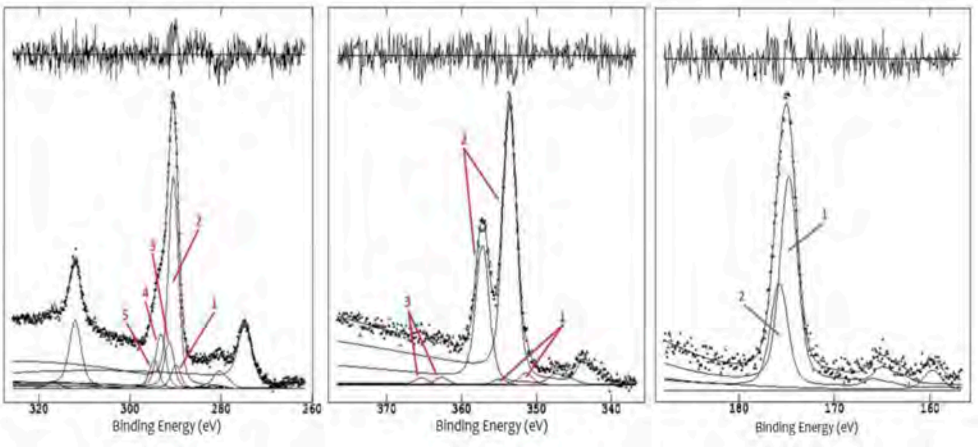


Figure 5. Main curve fitted regions of sample 1: C1s (left); Ca2p (centre) and S2p (right).

Table 1. Assignment of C1s and N1s peaks, corrected binding energies and attributions for sample #1.

C1s # Peak	BE corrected (eV)	Normalized Area	Assignments
1	284.5	1478.3	C-C
2	285.0	15582.0	C-C
3	285.9	3413.2	C-C-O, C-N, C-S
4	287.8	4020.7	C=O, O-C-O
5	289.2	2122.9	$(C_2O_4)^{2-}/(CO_3)^{2-}$
N1s	399.8	508	C-N

As evident in Figure 5, left, the whole acquired region comprises signals other than carbon: Cl2s and $MgKL_{2,3}L_{2,3}$ signals, at the extremes of the energy range, respectively contributing as secondary and Auger signal of the main 2p and Mg1s regions (vide infra).

Thus, only the five carbon peaks, resolved by curve-fitting the C1s region, are listed in Table 1. Peak n.1, in the lower BE range, includes carbides/cyclic carbons/ organic residues, specifically related to the degradation pathways found on masonry surfaces. Peak n. 2 is the aliphatic carbon signal (285.0 eV) which serves as an internal reference and allows to correct of all BE values. The aliphatic C1s peak theoretically falls at 285.0 eV, therefore, from the difference between the theoretical value and the experimental one, it is possible to calculate the charging factor and subtract it from all the BE values of the recorded signals. Peaks n. 3 and n. 4 are attributable to the presence of groups with (-C-O) /(-C-N) bonds and to ketone (-C=O) and/or (O-C-O) groups, respectively. The contribution of amine bonds is confirmed by the N1s region added in Table 1.

Peak n. 5 is attributable to carbon with multiple oxygen bonds, like carbonates of calcarenite stones and oxalates deriving from biodegradation (Scrano et al., 2020; Cardellicchio et al., 2023), respectively, both carbons contributing, sometimes unresolved by curve-fitting due to reciprocal chemical shifts induced by microbial activities, with different intensities in the narrow BE range of 289-290 eV (NIST, 2012; Cardellicchio, 2022).

In Table 2, the curve-fitted Ca2p region shows two different chemical states of calcium (Figure 5, center). The second doublet composed of $2p_{3/2}$ and $2p_{1/2}$ orbitals and shake-up satellites (the latter linked to intrinsic energy losses of 2p electrons), is strongly related to the doublet of the S2p region, relative to $2p_{3/2}$ and $2p_{1/2}$ orbitals, identified (Figure 5, right) as sulphate $(SO_4)^{2-}$as retrieved from the NIST database.

In the O1s region, two different component peaks were identified at 531.1 eV (corresponding to oxides of various metals including Mg and Ca) and at 532.5 eV (corresponding to other organic and inorganic oxygen species). As inferred from their assignments in Table 2, unresolved chemical states are contributing to both peaks, therefore, the O1s curve-fitted region is not so indicative qualitatively (figure not shown) and for the semi-quantitative analysis only the oxygen ‘total area’ was considered to perform the mass balance of all oxygen-containing compounds identified by comparing correlated spectral regions.

Table 2. Corrected binding energies and assignments of Ca2p, S2p and O1s peaks for sample #1.

Region	# Peak	BE corrected (eV)	Normalized area	Assignments
Ca2p	1	345.9	79.1	CaO
	1	349.4	41.5	CaO
	2	348.1	1811.6	$CaSO_4/CaC_2O_4/CaCO_3$
	2	351.7	905.8	$CaSO_4/CaC_2O_4/CaCO_3$
	3	357.2	53.3	*shake up*
	3	359.9	49.8	*shake up*
S2p	1	169.3	1464.7	$(SO_4)^{2-}/(CH_3)_2S$
	2	170.3	732.3	
O1s	1	531.1	1151.5	Metal oxides
	2	532.5	11314.1	$CaCO_3$, O-R

As well reported (Bonomo et al., 2020), calcarenite rock is mostly composed of calcite (sometimes associated with aragonite). Other components (magnesium carbonate, quartz, inorganic ions) may be present in different, minor percentages.

In Table 3, all remaining elements found in sample #1, are grouped under the heading "silicates", which indicates the silicate matrix, minority and often not stoichiometrically well defined, with impurities intrinsically sedimented or environmentally post-produced.

Table 3. Corrected binding energies and assignments of the silicate components in sample #1.

Peak	BE corrected (eV)	Normalized Area	Assignments
Mg1s	1305.0	1035	$MgO/Silicate/MgCl_2$
Cl2p	198.4	676	Chloride
Na1s	1072.7	226	$NaCl/Na_2SO_4$
Si2p	101.4/103.2	385	$SiC/SiO_x/SiO_2$

From the values of all normalized areas, obtained by curve fitting the acquired detailed regions, the atomic percentage composition (At%) of the identified species was calculated, based on partial mass balances (i.e. $Ca:SO_4/Ca:C_2O_4/Ca:CO_3$ for the main calcarenite components), on the overall neutrality balance and finally on the area ratio of the total oxygenated species with the O1s total area. In the limit of XPS accuracy (±10%, Briggs & Seah, 1990; Briggs & Grant, 2003), this data compilation makes it possible to carry out a semi-quantitative evaluation of the degradation products formed on the wall surfaces in relation to the location of samples. The results obtained are displayed in the pie charts shown below.

For sample #1, taken from a surface area of the wall in Figure 3 evidently degraded, the determination of the At% (Figure 6) shows that the vast majority is composed of carbonaceous components of different nature: 59% of C-C types (carbides, aliphatics, aromatic, etc) and 25% with other functionalities (C-S, C-O-C, C-O, C-N, C=O, etc). The presence of gypsum, calcium sulphate (7%), and calcium oxalate (4%) in the dark green patina composing sample #1 (see its location in Figure 3), can be associated with the transformation of calcium carbonate due to reactive sulphur compounds and of biological metabolites, respectively, as well documented for phenomena related to monumental degradation (Fassina, 1988; Gaylard et al., 2022).

The silicate components (SiOx), chlorides, and other alkaline earth metals, are linked together as suggested by the Auger parameter of magnesium for the three samples (α' = 2484.5 ± 0.5 eV), which is compatible with $MgCl_2$ and silicate minerals of the type $Na/Mg/Si_4O_{10}(OH)n$ (NIST, 2012). As exemplified in the pie chart of Figure 6, for this sample #1, the silicates/inorganic salts reach total a percentage of 5%.

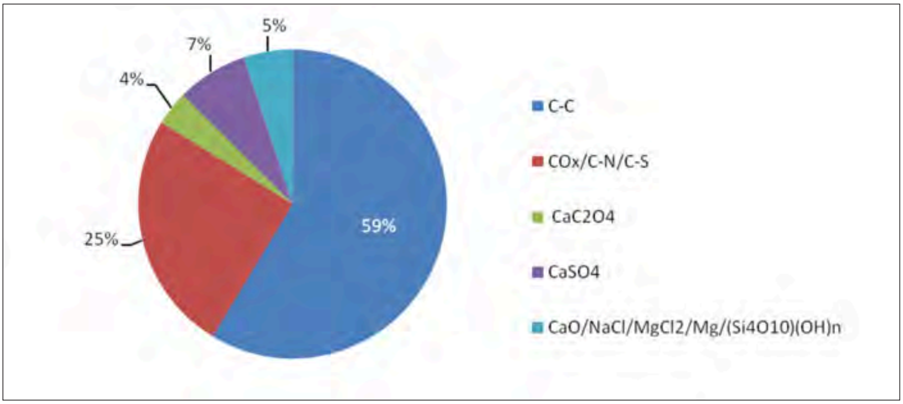


Figure 6. Percentage distribution of the various groups identified in sample #1.

The methods of analysis applied for sample #1 were then replicated for the other samples. For the sake of brevity, the wide and detailed spectra are not reported, but only the final results relating to the identified chemical species with their At% contribution.

Sample #3 was taken in an area visually less affected by degradation. This assessment is confirmed by the presence of a lower percentage of sulphate (1%) and by the concomitant higher percentage of calcium carbonate (23%), the main constituent of the calcarenitic material (Figure 7).

Similarly, the silicates percentage has increased to 13% also including a discrete amount of potassium, in addition to calcium as intercalated fluxing ions. Furthermore, the still high percentage of carbonaceous components testifies to the presence of biofilm residues, probably no longer bioactive, residing in the green patina that has expanded from the area of sample #1.

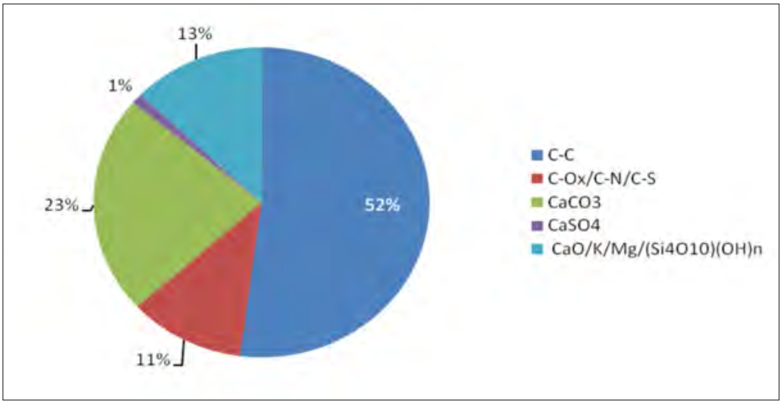


Figure 7. Percentage distribution of the various groups identified in sample #3.

As regards the last sample taken from the wall next to the high altar (sample #5), the analytical results summarized in Figure 8, show the same lower quantity of sulphates as for sample #3 and even an increase in the percentage of calcium carbonate (26%), as expected from a visual analysis (see Figure 3), given no more evidence of the dark green patinas on the wall surface. However, even in this whiter area, the percentage of the total organic carbon (62%) reaches that of sample 3, suggesting that bioactivity may also possibly derive from non-photosynthetic bacterial species which degrade the organic substance containing nitrogen, producing metabolites such as nitrates, present in this sample in an appreciable concentration (about 5.6% of the total percentage of the silicate group). In alternative or in addition, sodium and potassium nitrates can also be associated with efflorescence phenomena induced by water permeation/evaporation into the masonry.

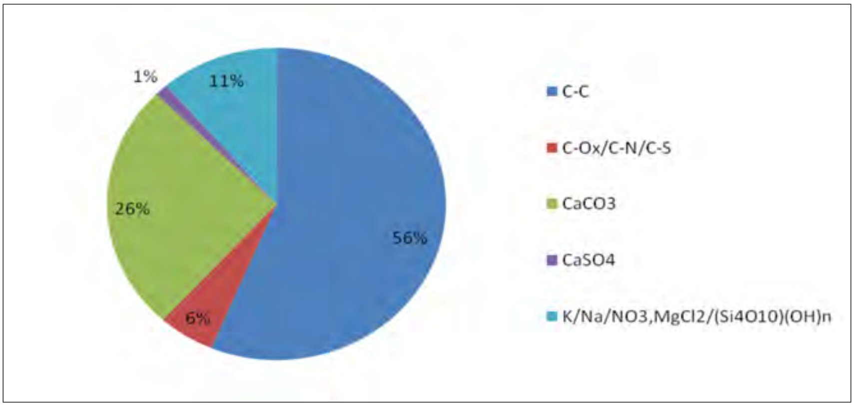


Figure 8. Percentage distribution of the various groups identified in sample #5.

In summary, along the diagnosed area, XPS investigation has proved the degradation phenomena to be linked both to the porosity of calcarenite and to environmental contaminants of biotic and abiotic origin:

- the transformation of the calcium carbonate mainly into gypsum and partly into calcium oxalate was highlighted in sample #1, the dark green bio-patina almost fully covering the right side of the wall in Figure 3.
- the appearance of calcium carbonate, characteristic of the calcarenite substrate and its progressively increasing percentage together with the silicate components going from sample #3 to sample #5 was found to follow the visible degree of the wall cleanliness.
- based on the total oxygen mass balance, sample #3 and #5 are more hydrated. The wall's hydration also progresses with the apparent discoloration of its surface probably due to the permeation of water, washing away the gypsum and the associated surface layers but also giving rise to phenomena of efflorescence, confirmed by the presence of magnesium and sodium salts at a different content in the three samples, eventually including $K/NaNO_3$ in sample #5.
- the ubiquitous presence of organic deposits on the wall surfaces, clearly highlighted by XPS, can be related to both atmospheric or water-driven contaminants and biometabolites, their coexistence particularly evident in sample #1, the colored patina.

Conclusions

In this work we have outlined the use of XPS, the surface spectroscopy dedicated to surface analysis, trying to explain quite in detail how the surface composition of any samples, representative of the case studies, can be provided using an appropriate curve-fitting procedure. As already demonstrated in previous work, the technique allows to define of an important cognitive framework and is of valid support as a diagnostic means of investigation also in the field of cultural heritage.

According to the SCN guidelines, the results obtained with XPS will be considered in concert with those provided by biological analyses, architectural and engineering surveys, and in general, by using complementary techniques and multi-laboratory experiments, altogether necessary to implement the technological platform, developed as part of the project such as an informative and scientific database.

As anticipated, the multivariate approach will be necessary for the control and containment of the multiple factors responsible for the degradation and biodegradation processes, offering an overview and providing the right indications for the planned maintenance and recovery interventions aimed at safeguarding stone monuments.

Acknowledgements

The SCN_00520 project supported by MIUR is acknowledged. We thank Dr. Mariangela Curcio for her contribution to the experiments related to San Pietro Barisano church.

References

AIES I.; L. Campanella - E. Dell'Aglio - R. Reale - F. Cardellicchio - A.M. Salvi - C. Casieri - G. Cerichelli - F. Gabriele - N. Spreti - G. Bernardo - A. Guida - V. Porcari, *Development of natural gels for cleaning the stone materials of cultural heritage from iron stains and biodeteriogenic microorganisms,* XII International Conference Diagnosis, Conservation and Enhancement of the Cultural Heritage, Naples 9-10 December 2021.

AIES II.: G. Bernardo - A. Guida - V. Porcari - L. Campanella - E. Dell'Aglio - R. Reale - F. Cardellicchio - A.M. Salvi - C. Casieri - G. Cerichelli - F. Gabriele - N. Spreti, *New materials and diagnostic techniques to prevent and control calcarenite degradation,* XII International Conference Diagnosis, Conservation and Enhancement of the Cultural Heritage, Naples 9-10 December 2021.

Bartoli F. - A.C. Municchia - Y. Futagami - H. Kashiwadani - K.H. Moon -G. Caneva, *Biological colonization patterns on the ruins of Angkor temples (Cambodia) in the biodeterioration vs bioprotection debate*, International Biodeterioration & Biodegradation. 96 (2014), pp. 157-165. http://dx.doi.org/10.1016/j.ibiod.2014.09.015

Bonazza A. - P. Messina - C. Sabbioni - C.M. Grossi - P. Brimblecombe, *Mapping the impact of climate change on surface recession of carbonate buildings in Europe,* Science of Total Environment, 407, (2009), pp. 2039 – 2050. https://doi.org/10.1016/j.scitotenv.2008.10.067

Bonomo, A.E.; Amodio, A.M.; Prosser, G.; Sileo, M.; Rizzo, G. Evaluation of soft limestone degradation in the Sassi UNESCO site (Matera, Southern Italy): loss of material measurement and classification. *Journal of Cultural Heritage*. 2020, 42, 191–201. https://doi.org/10.1016/j.culher.2019.07.017

Briggs D. - J.T. Grant, *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy,* IM Publications, Chichester, U.K., 1901019047, (2003) 900 pp.

Briggs D. – Seah M.P., *Practical Surface Analysis*; John Wiley & Sons, Chichester,UK,1990; ISBN0-471-26279-X.

Brimblecombe P., *Refining climate change threats to heritage,* J. Inst. Conserv., 37, (2014), 85–93. https://doi.org/10.1080/19455224.2014.916226

Cardellicchio F. - S.A. Bufo - S.M. Mang - I. Camele - A.M. Salvi - L. Scrano, *The bio-patina on a hypogeum wall of the Matera-Sassi rupestrianchurch "San Pietro Barisano" before and after treatment with glycoalkaloids, MDPI* Molecules, 2023, 28 (1), 330.

Cardellicchio, F., *Monitoring and conservation of stone cultural heritage: diagnostic investigations using surface techniques and innovative methodologies for sustainable maintenance interventions. Doctoral thesis*. 2022, 233 p. Not yet published.

Castle J.E. - A.M. Salvi, *Chemical state information from the near-peak region of the X ray photoelectron background*,, J. Electron Spectrosc. Relat. Phenom., 114-116, (2001) pp. 1103-1113. https://doi.org/10.1016/S0368-2048(00)00305-4

Castle J.E. - H. Chapman-Kpodo -A. Proctor -A.M. Salvi,*Curve-fitting in XPS using extrinsic and intrinsic background structure,* Journal of Electron Spectroscopy and Related Phenomena, 106(1), (2000), pp. 65-80. https://doi.org/10.1016/S0368-2048(99)00089-4

Charola A.E., *Salts in the Deterioration of Porous Materials: An Overview*, Journal of the American Institute for Conservation, 39 (3), (2000), pp. 327-343. https://doi.org/10.1179/019713600806113176

Coutinho M.L. - A.Z. Millerd - M.F. Macedo, *Biological colonization and biodeterioration of architectural ceramic materials: An overview*, Journal of Cultural Heritage, 16 (5), (2015), pp. 759–777. http://dx.doi.org/10.1016/j.culher.2015.01.006

Fassina V., *Environmental pollution in relation to stone decay, Durab.* Build. Mater. 1988, 5,317–358.

Gabriele F. - M. Tortora - L. Bruno - C. Casieri - M. Chiarini - R. Germani - N. Spreti, *Alginate-biocide hydrogel for the removal of biofilms from calcareous stone artworks*, Journal of Cultural Heritage 49, (2021), pp. 106–114. https://doi.org/10.1016/j.culher.2021.02.009

Gaylarde C. – Little B., *Biodeterioration of stone and metal-Fundamental microbial cycling processes with spatial and temporal scale differences*, Sci. Total Environ. 2022, 823,153193.

NIST, *X-ray Photoelectron Spectroscopy Database 20, Version 4*.1, (2012). https://srdata.nist.gov/xps/default.aspx.

Pauly B.D. - P. Schiffman - R.A. Zierenberg - D.A. Clague, *Environmental and chemical controls on palagonitization*, Geochemistry, Geophysics, Geosystems, 12(12), (2011), pp. 1-26. https://doi.org/10.1029/2011GC003639

Scrano L. - R. Laviano - G. Salzano - M. Santacroce - S.A. De Franchi - J. Baranek - S.A. Bufo, *Natural biocides and bio-calcite: innovative tools for cultural heritage,* Heritech 2020 IOP Conf. Series: Materials Science and Engineering 949, 012096, (2020) 10 pp. https://doi.org/10.1088/1757-899X/949/1/012096

Steiger M. - A.E. Charola - K. Sterflinger, Weathering and Deterioration in Stone in Architecture, Springer ed., (2011), pp. 227-316. https://doi.org/10.1007/978-3-642-14475-2_4

Tzanis C. - C. Varotsos - M. Ferm - J. Christodoulakis - M.N. Assimakopoulos - C. Efthymiou, *Nitric acid and particulate matter measurements at Athens, Greece, in connection with corrosion studies*, Atmospheric Chemistry and Physics, 9, (2009), pp. 8309–8316. https://doi.org/10.5194/acp-9-8309-2009

Urzì C. - P. Albertano, *Studying phototrophic and heterotrophic microbial communities on stone monuments*, in Doyle R.J (Eds.). Method Enzimol., 336, (2001), pp. 340-355.

CHEMOMETRIC LESSONS

Monica Casale

Introduction to Multivariate Analysis Techniques

Abstract

In this presentation, initially the group of analytical chemistry and chemometrics of the Department of Pharmacy of the University of Genoa is described, focusing on its research and teaching activities in the field of multivariate data analysis. In more detail, the research lines are presented together with the laboratory equipment available.

The basic techniques of multivariate analysis are then introduced and finally some applications of chemometrics are shown to solve real problems in different sectors, not only cultural heritage but clinical, food and environmental fields as well.

Keywords

Chemometrics; teaching activities; research lines; applications.

Riassunto

In questa presentazione, inizialmente viene descritto il gruppo di chimica analitica e chemiometrica del Dipartimento di Farmacia dell'Università di Genova, le sue attività di ricerca e insegnamento nel campo dell'analisi dei dati multivariati. Più in dettaglio, vengono presentate le linee di ricerca e la strumentazione di laboratorio disponibile.

Vengono quindi introdotte le tecniche di base dell'analisi multivariata e, infine, vengono mostrate alcune applicazioni della chemiometria per risolvere problemi reali in diversi settori, non solo dei beni culturali ma anche dal settore clinico a quello alimentare o ambientale.

Parole chiave

Chemiometria; attività didattiche; linee di ricerca; applicazioni.

Il gruppo di Ricerca di Chimica Analitica e Chemiometria del Dipartimento di Farmacia dell'Università di Genova

The Group of Analytical Chemistry and Chemometrics of the University of Genoa was founded in the early 1980s by Professor Michele Forina, within the Faculty of Pharmacy (now the Department of Pharmacy).

Chemometrics is the discipline that applies mathematical and statistical methods to process complex chemical data and extract useful information from them.

The research activity of the group focuses mainly on the application of innovative analytical approaches, based on vibrational spectroscopy, coupled with advanced chemometrics strategies involving both multivariate design of experiments (MDoE) and multivariate data processing (Pattern Recognition). The Genoa Group is, in fact, one of the few in the world with extensive experience in both fields of chemometrics.

Regarding vibrational spectroscopy, over the last few years, the Group's activity has focused on the use of portable devices and hyperspectral imaging. In particular, the Team is working on the development of analytical strategies dedicated to field applications and the monitoring of online processes.

As for imaging, the hyperspectral camera is used for the chemical mapping of compounds of interest in heterogeneous matrices that come from the most diverse sectors: not only cultural heritage but also food, forensic and environmental sciences.

Teaching is considered as a "vocation" by the Group, with the same importance of research activity, therefore all its members are regularly involved in the organization of schools and chemometric courses. To support the intensive teaching activity and, in particular, to provide free software to course participants, the Research Group is constantly involved in the development of chemometric packages with a simple graphic interface, to process complex chemical data and extract the contained information. Currently, the official software used by the Group is CAT (Chemometric Agile Tool) developed under the guidance of Professor Riccardo Leardi by a group of researchers including engineers, mathematicians and computer scientists. The CAT software is a standalone chemometric package containing functions for multivariate data analysis and experimental design, developed under the R environment.

Members of the research group also implemented a large number of chemometric methods as an opensource routine in the Matlab environment.

During this presentation some applications of Chemometrics have been shown, as examples, such as the development of (i) an analytical method based on fluorescence spectroscopy combined with multivariate data analysis for the early detection of prostate cancer through urine analysis, (ii) a multivariate classification method for the identification of mechanically separated meat in meat samples from ICP-MS analysis, (iii) an analytical method based on NIR spectroscopy for the characterisation of table olives of Taggiasca cultivar, (iiii) a strategy based on the use of NIR spectroscopy and Chemometrics methods for monitoring the mixing phase of a powder to determine the endpoint of the process.

Cristina Malegori

Principal Component Analysis (PCA): theoretical foundations, application principles and results' interpretation

Abstract

Principal Component Analysis is an exploratory chemometric technique, which allows to visualize multivariate data on a two-dimensional plane. The principal components are obtained by orthogonal rotation of the original variables and are the directions of maximum variance, that is maximum information. In this presentation the importance of data pre-treatment was also addressed.

Keywords

Chemometrics; PCA; display method; data pre-treatments.

Riassunto

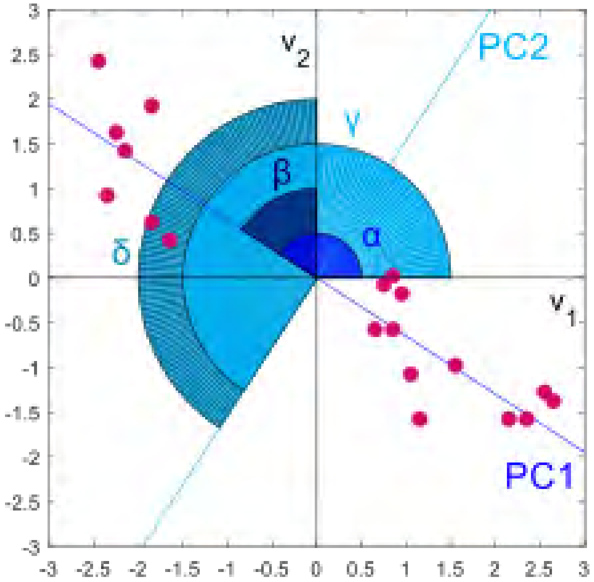
L'analisi delle componenti principali è una tecnica chemiometrica esplorativa, che consente di visualizzare dati multivariati su un piano bidimensionale. Le componenti principali sono ottenute per rotazione ortogonale delle variabili originali e sono le direzioni di massima varianza, cioè, massima informazione. In questa presentazione è stata anche affrontata l'importanza del pre-trattamento dei dati.

Parole chiave

Chemiometria; PCA; metodo di visualizzazione; pretrattamenti.

Principal Component Analysis

Principal Component Analysis (PCA) is an exploratory chemometric technique, which allows to view the collected data taking into account, simultaneously, all variables measured on each sample. This allows to explore the sample space to identify trends and groups and to study the structure of variance and covariance of variables. This joint interpretation between sample behaviour and correlation patterns between variables allows for a better visualization and interpretation of a data set that contains many correlated variables, reducing the size and maximizing the information contained in it.



PCA is based on the calculation of new variables, known as principal components (PCs), orthogonal and therefore uncorrelated. These variables are directions of maximum variance identified in the Cartesian plane defined by the original variables; the first PC shows the maximum information contained in the data, the second PC will be orthogonal to the first and will summarize the maximum information not explained by the previous component. The following components will be associated with a percentage of variance always lower. PCs are used to define a new Cartesian space called score space, where sample coordinates (scores) on the new axes can be displayed in pairs in two- or three-dimensional graphs, called score plots. PCA allows to trace the contributions of the original variables of the data set in establishing the PCs, called loadings, in order to study the relationship between samples and original variables and the correlation patterns between them. The absolute value of such loading defines the importance of the original variable in defining the PC while the sign defines the direction of correlation between the two variables.

It is also important to investigate how the comparability of variables of different nature is linked to a preliminary transformation of data. The most commonly used pretreatment is column centering with subsequent scaling (or studentization), when necessary, which eliminates a priori systematic differences in position and dispersion between the original variables, obtaining a set of pretreated variables, which are dimensionless, in which each transformed variable has average equal to 0 and variance equal to 1.

Paolo Oliveri

Multivariate Exploratory Analysis of RGB, Multispectral and Hyperspectral images

Abstract

In a multivariate system, like RGB, multispectral and hyperspectral images, it is fundamental to deal with methods that allow to explore the data structure in a visual way understanding typical characteristics, in terms of sample groupings and variable inter-correlations. Exploratory methods belong to the family of unsupervised strategies in which a-priori information about sample identity is neither required nor used for building models. Several methods, including cluster analysis, are available in this family but principal component analysis (PCA) is, for sure, the most widely employed. In the present contribution, application of PCA to multivariate image analysis (MIA) will be described, with a special focus on the pixel-based approach, on the unfolding/refolding procedures, and on exploratory brushing.

Keywords

Multivariate image analysis (MIA); principal component analysis (PCA); unfolding; refolding; brushing.

Riassunto

In un sistema multivariato, quali le immagini RGB, multispettrali e iperspettrali, è fondamentale disporre di metodi che consentano di esplorare la struttura dei dati in maniera visiva, comprendendone le caratteristiche essenziali in termini di raggruppamenti tra campioni e inter-correlazioni tra variabili. I metodi esplorativi appartengono alla famiglia delle strategie non supervisionate, in cui disporre di informazione a priori sull'identità dei campioni non è richiesto né funzionale alla costruzione dei modelli. Svariati metodi, inclusa l'analisi dei cluster, sono disponibili in questa famiglia, ma l'analisi delle componenti principali (PCA) è, senza dubbio, il metodo più utilizzato. Nel presente contributo, si descriverà l'applicazione della PCA all'analisi multivariata di immagini (MIA), con particolare riferimento all'approccio pixel-based, alle operazioni di unfolding/refolding e al brushing esplorativo.

Parole chiave

Analisi multivariate dell'immagine (MIA); analisi delle componenti principali (PCA); unfolding; refolding; brushing.

Multivariate Image Analysis

Hyperspectral data are usually stored in 3D data matrices, often referred to as hypercubes, in which rows and columns represent pixel position in the image, while the third dimension describes the spectral variables. Since PCA is applicable only on 2D data matrices, hypercubes have to be reorganised in a bi-dimensional structure prior to their processing; this procedure, called unfolding (Figure 1), can be performed following different schemes all aimed at having pixels as rows of the new matrix and variables as columns. A key point of this approach is the possibility of coming back to the original data organisation (refolding) by applying the inverse procedure (Figure 1). In such a way, the spatial information can be exploited for visualisation of PCA outcomes in a simple and incisive way.

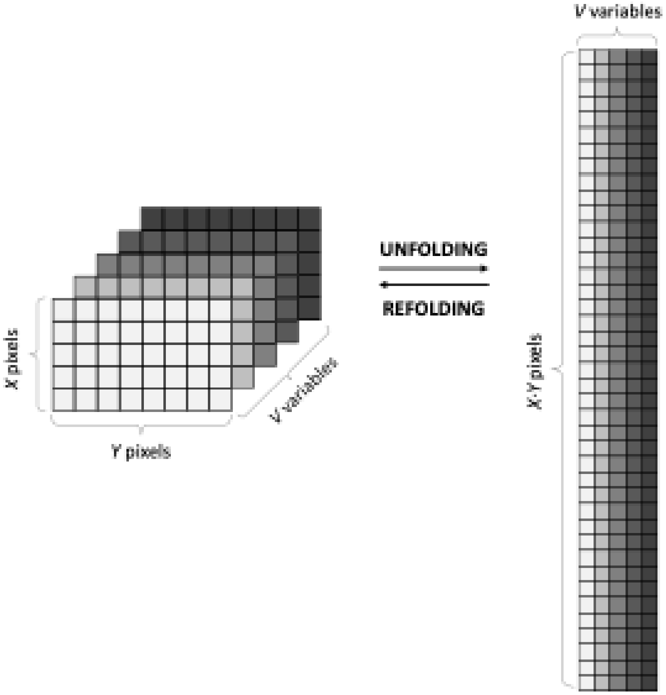


Figure 1. General scheme of an unfolding and refolding procedure for a 3D data cube.

When a hyperspectral image is submitted to multivariate data processing, including PCA, several approaches can be applied, depending not only on the type of data but also on the specific task that has to be achieved. In more detail, it has to be considered if the interesting information has to be looked for at an image level, at an object level or at a pixel level. In the first approach (image-based), the focus is on whole images, which are being studied and compared one respect to the others; narrowing the field of view, with the object-based approach, the focus is on single objects inside images; further narrowing the view, with the pixel-based approach, the focus is on individual pixels studied as single data points.

An approach is defined as pixel-based (or at the pixel level) when the differences among pixels express the useful information; in this case each pixel is described by its own spectral profile independently of the other pixels in the image. When this approach is followed, PCA is computed on a matrix structured with as many rows as pixels, obtained from the hypercube by unfolding. After PC computation, scores are obtained for each pixel, and can used both for drawing scatter score plots (in a Cartesian space defined by a couple of PCs) and for reconstructing score images/maps. In these maps, scores of a single PC of interest are refolded in the position corresponding to the related pixel in the image, allowing to visualise how the image areas are characterised by different intensity of scores. To do this, score values are coded by a given colour scale, either grey-scale or chromatic (e.g. from blue to red). Depending on the particular case under study, the useful information can be contained in higher order PCs because, in many cases, the lowest order PCs are associated with interfering information like illumination differences and physical roughness of sample surfaces. To understand if a given PC carries meaningfully arranged information, a recognisable pattern inside the score map has to be detected. Conversely, when a given score map shows randomly distributed patterns, this may indicate that the PC under examination is not associated with interesting information. When a score scatter plot is obtained from PCA at the pixel level, usually a huge number of points is represented inside the orthogonal space; in this case, the interest is rarely focused on a single pixel but clouds of pixels scattered along a component have to be identified and studied.

To understand the relationships among groupings of points in the score scatter plot and spatial regions in the score map, the so-called brushing procedure can be applied. Typically, brushing is performed by selecting a cluster of points of interest within the scatter plot: the algorithm automatically recognises the corresponding points (pixels) in the image and graphically highlights the matching region in the image. The procedure can be also performed in the opposite direction, by selecting spatial regions within the score image, and directly highlighting the corresponding points in the score scatter plot. The brushing approach is particularly useful, from an exploratory point of view, since it allows not only to understand relationships between areas in the score image and clusters in the score scatter plot, but also to determine the contribution of the spectral variables in characterising each region in the image. This last achievement is possible by jointly analysing score maps, score scatter plots and loading scatter plots – in which the importance of the original spectral variables in the definition of two given PCs is shown, as in any PCA application. Loading values, represented in a scatter way, give also information about inter-correlation among variables – the closer the loading values, the higher the correlation degree between a couple of variables. For a big amount of variables – a typical case for spectroscopic data – loadings can be represented as intensity profiles against the spectral variables, helping to easily visualise the contribution of each variable in constructing the new components. In fact, such a representation allows establishing a direct parallelism between spectral regions revealed as important by loading values and original absorption bands in spectral profiles.

Giorgia Sciutto

Application of multivariate techniques in the Cultural Heritage sector

Abstract

The application of chemometrics to cultural heritage, although relatively recent when compared to other sectors, has already shown to be of fundamental importance in the field for the evaluation of complex data. Thus, the complexity of the analytical data obtained from the investigation of artworks is induced by complexity of the materials (usually complex mixtures that change over time) and by the production of a considerable amount of data during a diagnostic campaign, due to the application of several complementary techniques. Chemometrics represents a key tool to support studies and researches in the field of conservation science addressing new urgent challenges related to the increasingly urgent need for new tools and strategies, which can be at the service of the interdisciplinary conservation community.

Keywords

Conservation science; Multivariate analysis; Spectral data.

Riassunto

L'applicazione della Chemiometria ai Beni Culturali, seppur relativamente recente se paragonata ad altri settori, ha già dimostrato essere di fondamentale importanza nell'ambito della scienza della conservazione per la valutazione di dati complessi. Infatti, la complessità dei dati analitici prodotti dall'indagine delle opere d'arte è da riferirsi a due aspetti: i) la complessità stessa dei materiali (solitamente miscele complesse che si modificano nel tempo); ii) l'elevata quantità di dati generati durante una campagna diagnostica, e dovuta all'applicazione di numerose tecniche complementari. La Chemiometria rappresenta uno strumento chiave per supportare studi e ricerche nel campo della scienza della conservazione affrontando nuove sfide proposte dalla sempre più urgente necessità di nuovi strumenti e strategie, che possano essere al servizio della comunità interdisciplinare della conservazione.

Parole chiave

Scienza della Conservazione; Analisi multivariata; Dati spettroscopici.

Chemometrics for Cultural Heritage

In the last decades, chemometrics has played a crucial role in the interpretation of analytical data and it has been increasingly employed in the conservation science, to overcome drawbacks and limitations related to the application of univariate approaches for the study of complex and heterogeneous matrices as those of the cultural heritage materials.

The complexity of the analytical data obtained from the investigation of cultural heritage is not only related to the complexity of the materials (usually complex mixtures that change over time) but also to the fact that often a single type of analytical technique is not adequate for a correct and complete characterization of an artwork.

Thus, the use of several complementary techniques is required, and this often leads to the production of a considerable amount of data produced during a diagnostic campaign.

It is also worth to note that the data obtained through analytical tools is not the same as information, but they may contain useful information, together with noise, superfluous and redundant information.

In order to correctly manipulate and interpret the data, suitable evaluation strategies are necessary that allow full understanding, as well as the removal of irrelevant information, also allowing a data reduction.

Univariate analysis is the simplest form of analysing data, considering one variable at a time independently of the others, without taking into account intercorrelation between variables – a feature that can be very informative, if recognised and properly interpreted. By using univariate approaches, several problems may arise, related to the presence of complex mixtures, which may affect the correct identification and localisation of the compounds. Thus, it has been widely demonstrated that, when data sets are constituted by multiple objects and inter-correlated variables, univariate methods – which examine one variable at a time – considerably underutilise the information enclosed therein. Conversely, multivariate approaches are able to consider and represent the whole information in an easily understandable way.

Within this scenario, chemometrics represents a key tool to support studies and researches in the field of conservation science.

The first publication relating to the application of chemometrics in the field of cultural heritage dates back to 1998(*Musumarra, G., and Fichera M. "Chemometrics and cultural heritage." Chemometrics and intelligent laboratory systems 44.1-2: 363-372*). Subsequently, the number of works traceable in the literature has grown considerably, especially in the last twenty years.

If this has been leading by a new awareness, on the other hand, it is now more than ever necessary to deal with the correct training of scientists and operators, to create a new scientific community which is able to properly applied chemometrics tools and fully interpretate outcomes, addressing conservation issues.

Indeed, an appropriate use of chemometric tools refers to the overall analytical approach: from the definition of the problem to the choice of samples and the type of analysis.

Among the most widely used tools in the field of cultural heritage there is certainly the PCA, an exploratory multivariate analysis that allows you to maximize the information contained in the data, looking for their maximum variability.

In particular, the technique has proved to be very useful for the evaluation of spectroscopic data obtained through the use of spectroscopies operating in different spectral ranges (X-Ray Fluorescence, Near and Mid Infrared spectroscopy and microscopy), where problems related to bands deformation and overlapping, as well as changes in relative intensities of analytical signals may occur, hampering a correct evaluation of big datasets.

Nowadays, conservation scientists are also called to address new challenges related to the increasingly urgent need for new tools and strategies, which can be at the service of the interdisciplinary conservation community, for: (i) the prompt and efficient characterization of artworks components; (ii) the selection of proper conservation strategies; (iii) the reduction of response time and cost of analysis; (iv) the support the application of correct procedures in restoration campaigns.

With these aims, multivariate methods can play a crucial role for the development of adequate and increasingly automated tools available to the entire community.

INNOVATIVE EQUIPMENT

Introduction to EnviroESCA the Near-Ambient Pressure-XPS

The XPS technique for surface analysis is now well known, used in many scientific disciplines and the number of machines installed, even in Italy, is now considerable. Despite being a formidable instrument, the XPS suffers from a major limitation, namely that it is only possible to analyze samples compatible with the ultra-high vacuum (UHV, typically better than 10-9 mbar) into which the samples must be placed. To overcome this limitation and make the technique usable on a greater variety of samples, in recent years the so-called NAP- XPS systems, have been developed, in which the analysis chamber is no longer maintained in ultra-high vacuum but at a pressure which can even reach 100 mbar. The pioneer of this technique was the German company SPECS which has been developing components and systems for XPS for decades. Early NAP- XPS systems required X-ray fluxes available only in ultra-bright sources, such as synchrotrons. Precisely for this reason, the first NAP systems were created with special analyzers mounted on the beamlines of various synchrotrons. Over time, traditional X-ray sources have improved and, especially when photons are focused on a small spot, have achieved sufficient fluxes to allow the development of autonomous, synchrotron-independent NAP-XPS systems. Although the technique is not yet particularly known, except in some limited areas, it has opened up its applicability to many samples and has made possible operand measurements that were simply not feasible before. For example, the first applications on biological samples are starting to appear, even if they are only in their infancy. The applications in the field of catalysis and electrochemistry are probably better known, where in fact operand measurements are already possible. The technique can now also be used for samples that could be damaged by an ultra-high vacuum environment, such as any archaeological finds, the subject of the note from SPECS on EnviroESCA published here.

Pra.Ma. products presented at the Workshop

SPECS products are distributed in Italy by the Pra.Ma group: http://www.pra-ma.com/index.php/en/ which also distributes the products of the following companies:

- Alemnis, a Swiss company that manufactures instruments for measuring the micro and nanomechanical properties of materials.
- CHI-VAC, a Chinese company specialized in the production of vacuum components.
- Hiden Analytical, a British company specializing in quadrupole mass spectrometers, residual gas analyzers and SIMS systems.
- Korvus Technology, a British company specialized in thin film deposition systems.
- Kratos Analytical, a British manufacturer of ultra-high vacuum XPS systems characterized by a high degree of automation.
- NT-MDT, a Dutch company specialized in the creation of Atomic Force Microscopes.
- Rtec-Instruments, a US company that develops and produces advanced solutions for tribological tests and measurement of surface properties.
- SOL Instruments, a Belarusian company focused on Raman Microscopy, Elemental Analysis and Spectroscopy.

EnviroESCA applications in Scientific Archaeology

This application note presents the application of EnviroESCA to the field of Archaeometry. Besides the ability of Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS) to analyze the surface composition of metallic and nonmetallic specimens, EnviroESCA allows for a nondestructive analysis of artifacts without special pretreatment procedures.

Motivation

When it comes to the analysis of ancient artifacts the first methods that come to mind are based on photo-optical techniques. First of all because they can mostly be applied to artifacts of all sizes and do not harm or destroy the specimens. Surface Science techniques that require vacuum in machines that can only handle relatively small portions of the relics are powerful methods that allow determining the surface composition of the specimen. But these techniques require the samples to be vacuum compatible, to not out-gas, to be cut in pieces or small chunks. Until now. EnviroESCA is the next generation tool for Photoelectron Spectroscopy with X-rays (XPS) in Archaeometry and Scientific Archaeology as is accepts samples with a maximum diameter of 120 mm whereas the inner 28 cm^2 (circle of 60mm dia.) of the specimen can be analyzed. EnviroESCA does not require high vacuum or ultra-high vacuum to operate as it can also operate in pressures up to 100 mbar, it does not require the specimen to be cleaned with divergent or other chemicals, blowing of loose particles with dry nitrogen gas or dry air is sufficient. Due to an intrinsic charge compensation effect the operator does not bother with charge compensation equipment for almost all samples independent of their type, metallic, non-metallic, ceramic, organic,organometallic or even liquid. The samples can be laid flat without gluing or mechanical fixing (dependent on the weight of the sample) onto the sample stage.

For very sensitive samples humidified air can be supplied during the analysis along with other inert gases if needed. After the non-destructive analysis with XPS the sample can be directly brought back to the collection in the exhibition hall or handed over to the collector.

Fig. 1. Roman coin showing the face of Licinivs (308-324 A.D).

Method

EnviroESCA utilizes X-ray Photoelectron Spectroscopy (XPS) as its main analytical technique.

Hereby an electron beam is generated inside the X-ray These electrons propagate through the lens system of source and focused onto an X-ray anode made of Aluminum. The deceleration of the electrons on the anode leads to the production of X-rays.

This X-ray beam is monochromated and focused onto the sample.

X-ray photons impinging the sample excite electrons in the material which are subsequently emitted with specific kinetic energy determined by their binding energy and the photon energy of the X-rays.

Thereby only electrons from atoms up to a depth of 10 nm are able to leave the surface.

These electrons propagate through the lens system of Electron Analyzer into the hemisphere which acts as a spherical capacitor forcing the electrons onto circular paths with radii depending on their kinetic energy. The electron paths end at an electron sensitive detector where the electrons are amplified and measured as an intensity in counts / second. Sweeping the voltage of the spherical capacitor while measuring the number of electrons per second on the detector results in a photoelectron spectrum. From these spectra a quantitative analysis of the atomic composition of the sample surface can be done.

An intrinsic charge compensation method which we call Environmental Charge Compensation makes additional electron or ion sources for charge compensation as in classical XPS systems unnecessary. The gas atmosphere that is surrounding the specimen delivers all the free charges, when illuminated with the soft X-rays, that are needed to compensate for surface charging (see figure 2 for an illustration).

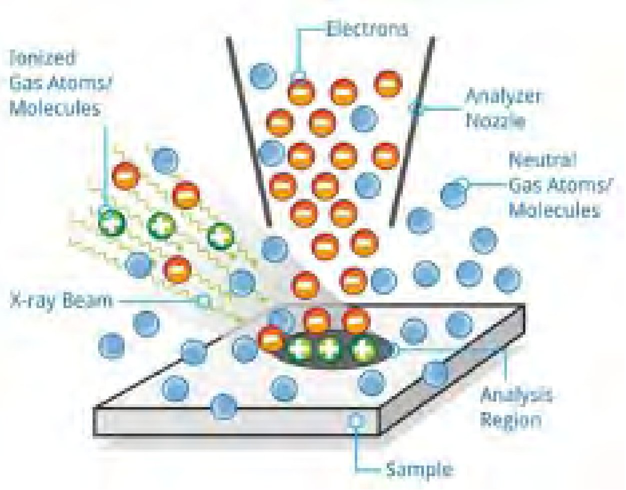


Fig. 2. Environmental Charge Compensation.

Experimental Section

For this investigation we have been offered an ancient roman coin from a local collector. The coin is dated 313-314 A.D. and is currently more than 1700 years old. The coin itself has a gray and partly green patina with small orange spots and exposes blank metal at several positions.

Loose dust and particles were removed by blowing gaseous nitrogen across the surface of the coin before it was put on the sample plate. No gluing or mechanical fixing in any way and also no electrical contacting or masking were applied.

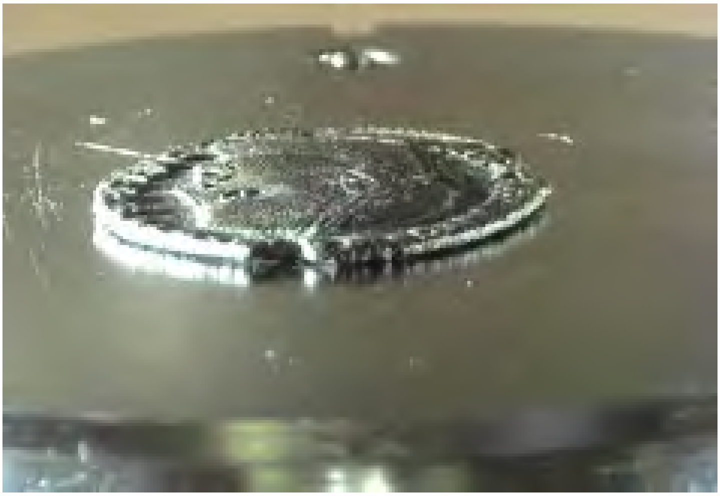


Fig. 3. The coin loosely positioned on the sample plate in the Sample Environment.

Measurement positions were selected on both sides of the coin and are shown in figure 4.

For the first measurements the exposed surface close to the hand of the displayed person was chosen. The second position is close to the edge of the coin at an orange spot. The third measurement position was placed on the front side of the coin at the end of the nose of the image of Licinivs.

Because the electrical contact to the sample plate differs depending on which side of the coin is establishing the contact we have shifted all following spectra for comparison in a way that Carbon 1s peaks in different spectra are located at 284.5eV.

Fig. 4. The three measurement positions.

Because of the thick patina charging up of the specimen under the illumination with X-rays was expected.

To address this circumstance a working pressure of 1 mbar ambient air was chosen so that the binding energy shift in the spectra due to charging effects were negligible (only 2.45 eV).

As these coins are known to be made of alloys of metals that were available at this time, survey spectra with longer acquisition time were measured on each position before regions in the energy spectrum were selected for the recording of detail spectra.

Results

In the following unmodified raw data taken with EnviroESCA will be presented. The data was not smoothened. For comparison the spectra were shifted on the energy scale so that the Carbon 1s peak on all survey spectra is located at 284.5 eV, as mentioned above.

1st Position

After pumping down of the Sample Environment to about 1 mbar the data acquisition was started which delivered the survey spectrum of figure 5.

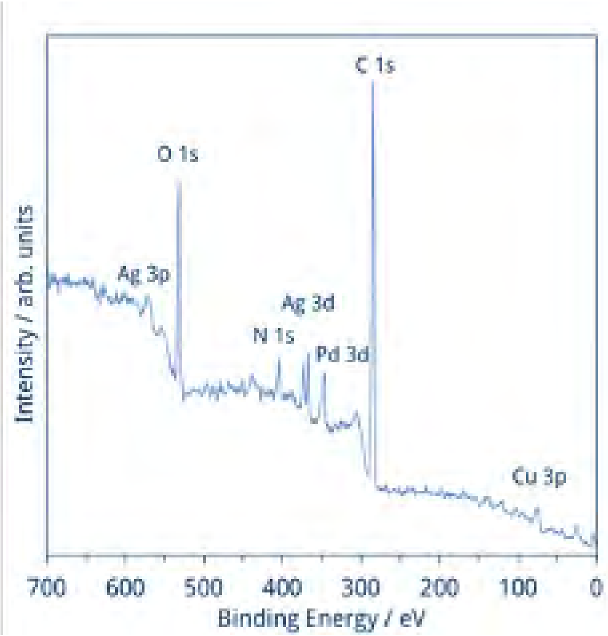


Fig. 5. Survey XPS spectrum recorded at position 1.

This spectrum was recorded in 12 minutes and 25 seconds with a step width of 1 eV. The spectrum shows clear evidence of Silver and Copper besides large Oxygen, Nitrogen and Carbon 1s core level peaks. Peaks resulting from electrons escaping Palladium atoms are also visible.

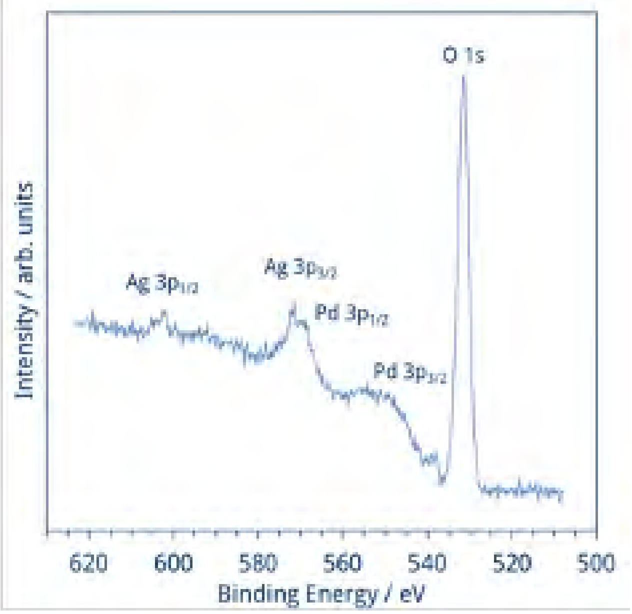


Fig. 6. A closer look at the Oxygen 1s region.

A closer look at the Oxygen 1s region (see fig 6) shows a light oxidation of the silver as the Ag 3p peaks exhibiting shoulders on the higher binding energy side. The low energy shoulder of the Ag $3p_{3/2}$ peak results from the Palladium $3p_{1/2}$ core level excitation.

The spectrum displayed in figure 9 is a detailed view at the Carbon 1s region on the spectra where besides the intense Carbon 1s the split 3d peaks of Silver and Palladium can be seen. The sharp Nitrogen 1s core level emission is due to the ambient air gas phase surrounding the specimen in this experiment. The spectra is the result of 5 scans of this region with a step width of 0.2 eV and a total measurement time of 17 minutes and 13 seconds.

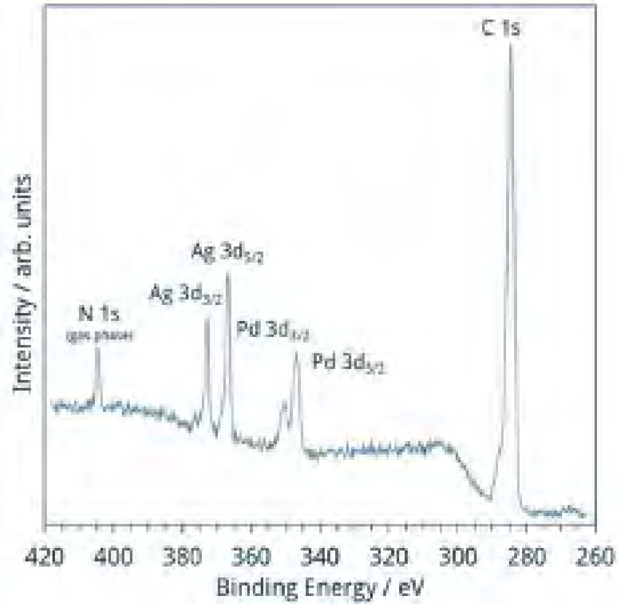


Fig. 7. Detail view at the Carbon 1s region.

The valence band spectrum recorded at this position shows peak structures related to Copper, Lead, Palladium and Sulfur (see figure 8 for details).

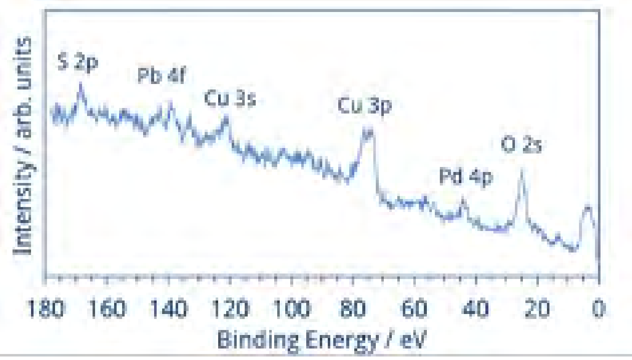


Fig. 8. Valence band spectrum recorded at position 1.

2nd Position

The survey spectrum recorded at the second position at the edge of the coin reveals Silicon core level peaks (2s and 2p) in addition to the peaks of the metals also found at position 1.

The detection of signals belonging to Silicon can be due to sand that was not removed by the cleaning with dry nitrogen. Nevertheless the valence band spectrum shown in figure 12 shows a nicely split Lead 4f peak in between the Silicon 2s and 2p core level peaks.

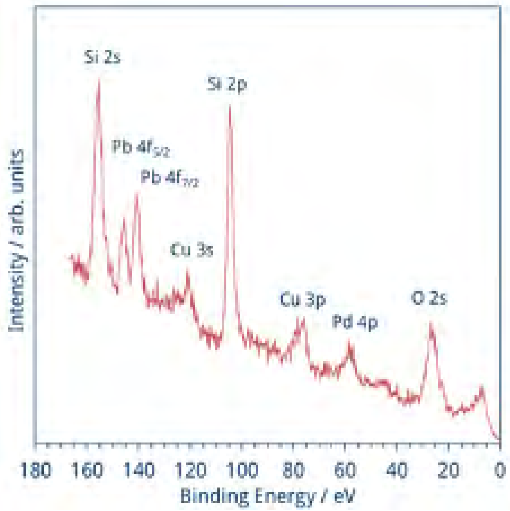


Fig. 9. Valence band spectrum recorded in about 20 minutes.

3rd Position

For the third measurement position a site on the front side was chosen. Because a position at the tip of the nose caught the eye with a metallic luster the position shown in figure 13 was selected.

The survey spectrum measured at this position shows more pronounced Silver peaks than in the other survey spectra (figure 10). In addition a peak resulting from Tin on the surface is visible (Sn 3d).

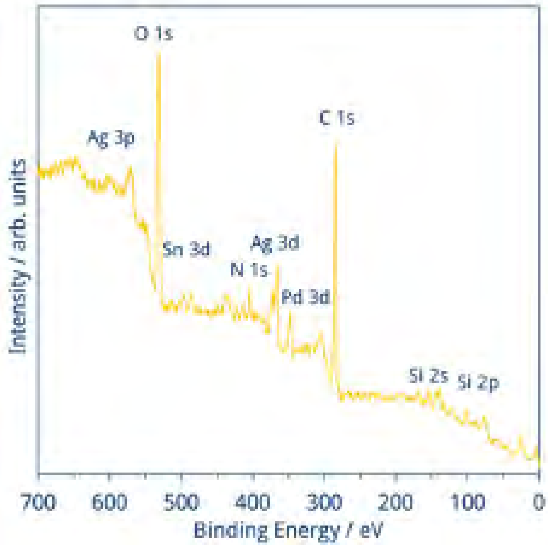


Fig. 10. Survey spectrum measured at position 3.

A closer look at this region presents signals from metallic Silver and oxidized Silver on the surface resulting in the shift of the split Silver 3d peak towards higher binding energies.

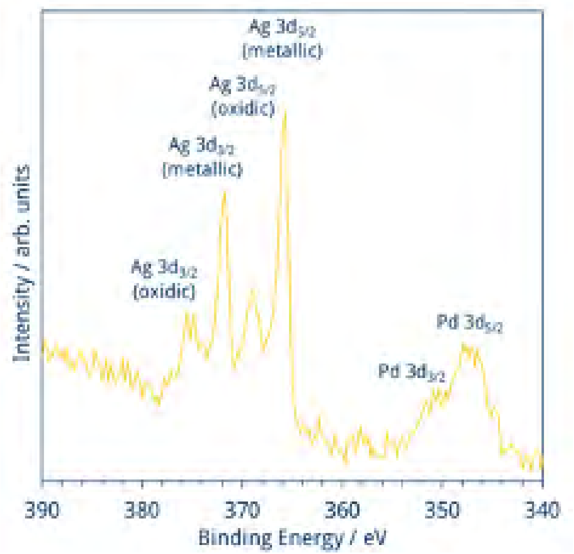


Fig. 11. Silver 3d region of the spectrum.

Conclusions

EnviroESCA using Near Ambient Pressure X-Ray Photoelectron Spectroscopy (NAP-XPS) or Ambient PressureXPS (AP-XPS) as it is also called has shown its ability in the analysis and characterization of the surface composition of artifacts without the need to damage or destroy them for data acquisition.

Even on a sample with a thick patina it was easy to find sites on the faces of the coin for analyzing the metal surface. The small spot size of the X-ray source of the EnviroESCA comes in handy to suppress the signal of the surrounding patina and organic residues.

We were able to provide evidence that the coin was made up of a bronze consisting of the following metals: Silver, Lead, Copper, Tin and Palladium.

1982 — 2022
UNIVERSITÀ
DEGLI STUDI DELLA
BASILICATA

Dipartimento di Scienze

Christmas Workshop

Imaging spettroscopico e chemiometria per la caratterizzazione di materiali di interesse artistico e culturale

15 – 16 Dicembre 2022
Aula B 003
Università degli Studi della Basilicata
Via Lanera, 20 – Matera

Il Workshop è rivolto a ricercatori, dottorandi e giovani laureati UniBas che svolgono la loro attività in ateneo e/o presso enti, istituzioni di ricerca e realtà industriali della Regione Basilicata. Intende approfondire i metodi di analisi chemiometrica per estrarre la massima informazione dai dati sperimentali, con particolare riferimento all'imaging spettroscopico, per una rappresentazione grafica ed efficace

(http://www.iupac.org/publications/pac/pdf/1983/pdf/5512x1861.pdf)

La partecipazione **è gratuita**, previo invio della scheda di registrazione tramite email entro il 9 Dicembre al Comitato Organizzatore che provvederà a fornire tutte le informazioni utili per la frequenza delle lezioni teoriche e pratiche.

Comitato Organizzatore

Anna Maria Salvi - anna.salvi@unibas.it
Graziella Bernardo - graziella.bernardo@unibas.it
Maria Assunta Acquavia - maria.acquavia@unibas.it
Francesco Cardellicchio - francesco.cardellicchio@imaa.cnr.it
Francesca Visone - francesca.visone@unibas.it

Programma Scientifico

15 Dicembre 2022

09:00-10:00
Registrazioni e Apertura del Workshop a cura del Comitato organizzatore
Saluti di Benvenuto:
Aldo Corcella (DiCEM), Roberto Teghil (DiS)
Introduzione ai lavori scientifici:
Antonella Guida (UniBas)
Sabino A. Bufo (UniBas)
Fausto Villani (TAB Consulting S.r.l.)

10:00-10:40
Vito D. Porcari (UniBas):
La manutenzione dei Beni Culturali. Azioni e strategie di un processo programmato per la valorizzazione del patrimonio architettonico

Paola Di Leo (IMAA-CNR, UniBas):
Micro X-ray fluorescence imaging e caratterizzazione chimico-mineralogica di pigmenti nei materiali di interesse artistico-culturale

Graziella Bernardo (UniBas):
Materiali green e metodi diagnostici non invasivi per la conservazione sostenibile del patrimonio architettonico

10:40-11:00
Carmine Schiavone (TAB Consulting S.r.l.):
He-Main. Piattaforma informativa per la gestione e manutenzione dei Beni Culturali

11:00-11:20
Angela De Bonis (UniBas):
Spettroscopie laser per i Beni Culturali: caratterizzazione di materiali metallici e lapidei

11:20-11:40 Coffee Break

11:40-12:00
Giovanna Rizzo,
Roberto Buccione (UniBas):
Approccio petrografico, mineralogico e geochimico applicato ai Beni Culturali

12:00-12:20
Laura Scrano (UniBas):
BIO-Strategie innovative per il ‘cleaning’ e la ‘restoration’ del patrimonio lapideo e metallico

12:20-12:40
Nicola Cardellicchio (UniBas):
L’impatto del cambiamento climatico sui Beni Culturali

12:40-13:00
Francesco Cardellicchio (IMAA-CNR):
Impiego di tecniche di analisi di superficie per la diagnostica del degrado dei Beni Culturali

13:00– 14.30 Pausa Pranzo

14.30- 16.00
Monica Casale (UniGe):
Introduzione alle tecniche di analisi multivariata

16:00-16:30 Coffee Break

16.30-18:00
Giorgia Sciutto (UniBO):
Applicazioni di tecniche di analisi multivariata nel settore dei Beni Culturali

16 Dicembre 2022

09.30 - 11:00
Cristina Malegori (UniGe):
Analisi delle componenti principali (PCA): fondamenti teorici, principi applicativi e interpretazione dei risultati

11:00-11:30 Coffee Break

11:30-13:00
Paolo Oliveri (UniGe):
Analisi multivariata esplorativa di immagini RGB, multispettrali e iperspettrali

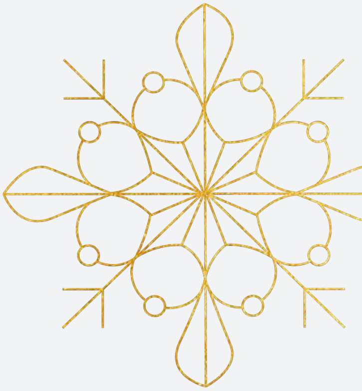
13:00- 14.30 Pausa Pranzo

14.30- 16:00
Monica Casale,
Cristina Malegori (UniGe):
CAT - Chemometric Agile Tool: esercitazione guidata

16:00- 16.30 Coffee Break

16:30-18:00
Paolo Oliveri (UniGe),
Giorgia Sciutto (UniBO):
Polibrush for image analysis: esercitazione guidata

18:00 Saluti e chiusura del Workshop



Si ringraziano per il contributo e il supporto alla organizzazione

SPECS™ Pra.Ma.GROUP

Durante le pause del workshop sarà visitabile la postazione del Dr. Mario Da Prada per informazioni e dimostrazioni su 'Imaging- e NAP-XPS' e ultimi prodotti SPECS con applicazioni di microscopia nell'ambito dei Beni Culturali - https://www.specs-group.com/

UniGe | DIFAR

Progetto di Ricerca Curiosity Driven 2020 "3Depth – From 2D to 3D hyperspectral imaging exploiting the penetration depth of near-infrared radiation"

This Volume collects all the dissemination contributions presented at the Christmas Workshop devoted to chemometric analysis for the processing of experimental data, with particular reference to spectroscopic imaging. The training objective was achieved and all the participants were provided with the necessary technical supports and software needed to follow the lessons and demonstration exercises held by expert teachers in multivariate analysis. The lectures addressed the topic of caring and preserving environmental and cultural heritages, highlighting the importance of diagnostics, the use of integrated and innovative techniques, and advanced statistic for data interpretation. Overall, the Volume is the results of the synergistic cooperation between different disciplines, too surreptitiously classified into humanities and technical-scientific.

PhD. ANNA MARIA SALVI. Associate Professor- CHIM/01 - Analytical Chemistry (https://orcid.org/0000-0001-7990-8764). The research activity, based on the combined use of XPS and other microscopic and analytical techniques, is related to the surface characterization of materials of biological, environmental and technological importance with special emphasis to XPS data elaboration. Over 80 publications, ISI journals and peer reviewed long-abstract and as many Congress contribution were produced, available onsite: Iris/UniBas database http://docenti.unibas.it/site/home.html.

PhD. Eng. GRAZIELLA BERNARDO. University Researcher- ICAR/10 - Building Technology and Design (http://orcid.org/0000-0001-9291-6099). Since 2012, teaching and research activities at the Department of European and Mediterranean Cultures are devoted to the sustainability of building processes and to the recovery and enhancement of cultural heritage. Most of the publications are conference proceedings, chapters in volumes and papers of international journals, available onsite: Iris/UniBas database http://docenti.unibas.it/site/home.html.

Prof. ANTONELLA GUIDA. Architect and Full Professor- ICAR/10 - Building Technology and Design (https://orcid.org/0000-0003-3419-9831). The scientific interest, oriented to the technical-technological aspects of urban construction processes, comprises experimental investigations aimed at the recovery of the existing cultural and industrial building heritages, application of innovative ICT technologies and enhancement/redevelopment of historic centres. At a professional level, consultancy activities for administrations and public bodies and professional assignments are provided on these issues. The scientific production consists of over 200 publications on peer reviewed journals, books and proceedings of national and international conferences, available onsite: Iris/UniBas database http://docenti.unibas.it/site/home.html.

ISBN 978-88-31309-21-9

9 788831 309219