Chemistry and Cultural Heritage*

For long term preservation of cultural heritage, the development of effective and sustainable conservation materials is fundamental. In this issue, innovative methodologies developed for cleaning are discussed (detail from a stained glass, D. Fernando II collection, Parques Sintra – Monte da Lua).

by Maria J. Melo, Austin Nevin and Piero Baglioni

"...il n'est pas possible de bien conserver ce que l'on connait mal" -Louis Pasteur

Made to measure

The conservation of works of art makes them accessible, and will ensure the transfer of cultural heritage to future generations,. For long term preservation, the development of effective and sustainable conservation materials is of fundamental importance. Although in the past traditional approaches in restoration have used highly effective natural materials for cleaning, modern research has focused on the systematic design of materials and methodologies. For instance, during the nineteenth century conservators reported the use of materials such as vinegar, wine, lemon juice, and today saliva is still used in cleaning applications. Although it is now recognized that these materials contain components that are effective cleaning agents, until recently there has been a lack of systematic studies regarding the control of their structure and reactivity.

The last 50 years have witnessed major advancements in conservation science [1, 2]. Many efforts have been dedicated to the development of analytical techniques for the study of artifacts, but significantly less research has focused on the design of innovative materials and methods for the remedial conservation of works of art, which includes cleaning. In this sense, colloids and materials science have provided valuable novel systems for the cleaning, protection and consolidation of cultural heritage objects. The key feature of newly developed materials is that they are designed and engineered to have enhanced effectiveness while showing physical chemical properties similar to the original artifacts. This allows one to minimize drawbacks or negative impacts, in the long-term, following treatment of the works.

Starting from the aftermath of the Florence and Venice floods in the late 1960s, which threatened significant masterpieces, many systems, including nanoparticles, microemulsions and gels, were specifically designed and applied to counteract the degradation processes that affected the artifacts. These new solutions have proved more effective and compatible than synthetic and macromolecular materials (*e.g.* polymeric adhesives and coatings), and guidelines have been described to help conservators in the use of advanced tools. Recently, the palette of conservation materials has expanded significantly as the critical conservation issues of modern and contemporary art become apparent.

A closer look

The field of Chemistry for Conservation is vast and it encompasses analysis, materials characterization, degradation studies, surface science and the development

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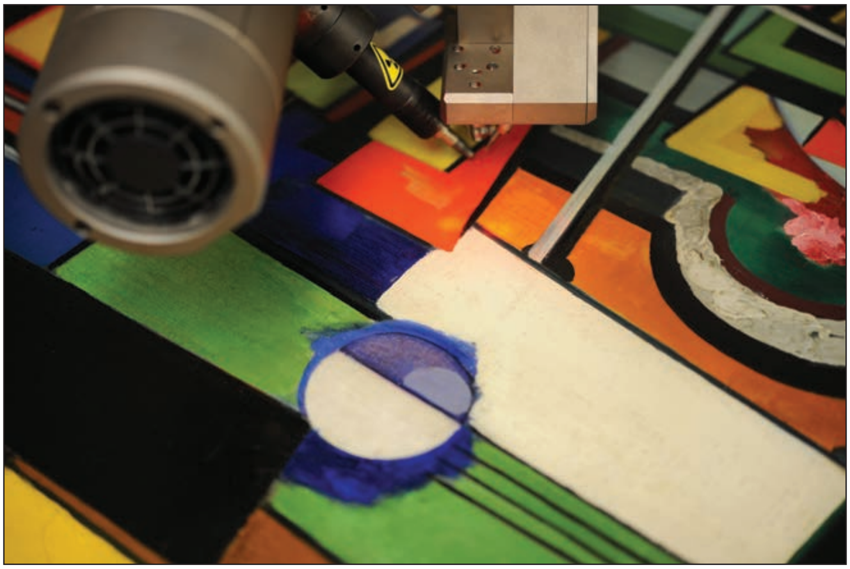
and synthesis of novel materials for conservation. A key part of conservation is the necessary understanding of the materials which make up works of art, very few of which are simple. Indeed it is not uncommon to find a heterogeneous mixture of organic and inorganic materials, whether animal or vegetal binders, pigments, dyes, fibers, macromolecules, polymers, minerals, semiconductors, alloys or metals when examining a work of art. Contemporary art, and the range of plastics and additives which have been used over the last century, poses particularly difficult challenges to conservators and scientists due to the intrinsic susceptibility of materials to degradation, much of which remains poorly understood. Whether ancient of modern, materials, and the ways they have been manipulated, synthesized and employed, all contribute to this unique physical record of our past. Indeed, the complexity of constituent materials makes the study of art a fascinating challenge, and various approaches have been developed for the examination of our cultural heritage.

It is useful here to remind the reader that Conservation generally aims to establish (a) whether or not a work is at risk, (b) if degradation is ongoing, or (c) if degradation has occurred but is no longer progressing. If intervention is necessary, it becomes critical to establish suitable methods for stabilization or consolidation, cleaning, and, often, protection. Chemistry can, therefore, play a key role in providing data to answer these questions, whether through the identification of materials, some of which could degrade, to the detection of oxidation or similar degradation reactions, to the development of new methods and materials.

As detailed in the Glossary provided as Supporting Information to the *PAC* Preface (https://doi.org/10.1515/pac-2018-0106), much of the study of works of art can be achieved without sampling—a particularly relevant issue for the vast majority of heritage which is immovable. Great strides have been made in the development of instrumentation and the application of portable techniques for the study of works of art and their degradation, and methods and tools are becoming increasingly available in major research centers, but may remain inaccessible for many collections and conservators. Current trends in the field include the study of model materials and their degradation with increasingly complex methods for the characterisation of degradation mechanismsˆusing both theory and experimental data. Preventive conservation relies on the elimination of factors which lead to degradation. The integration of data from different, often multiple, analytical techniques on different scales—from microanalysis to the study of large surfaces with imaging techniques—is becoming more common, especially for the analysis of easel paintings.

Even when instrumentation and methods can travel to an object, whether wall paintings in a grotto, religious buildings, monuments, or museums, for example, it is not always possible to answer some of the key questions posed by conservators specifically for conservation without careful sampling and suitable study with reasonable analytical techniques. Internationally, conservation scientists strive to answer conservation-driven questions, where the integrity of an object should be the ultimate aim. When instrumentation cannot travel, or when questions are sufficiently motivated, sampling may be necessary. Micro-sampling techniques thus pose a key advantage and are increasingly used in studies—indeed, invisible detection and

The understanding of the materials which make up works of art is key for conservation. Advanced analytical techniques are applied to characterize the materials aiming to establish whether a work is at risk (detail from a painting of Amadeo de Souza-Cardoso, Fundação Calouste Gulbenkian collection).



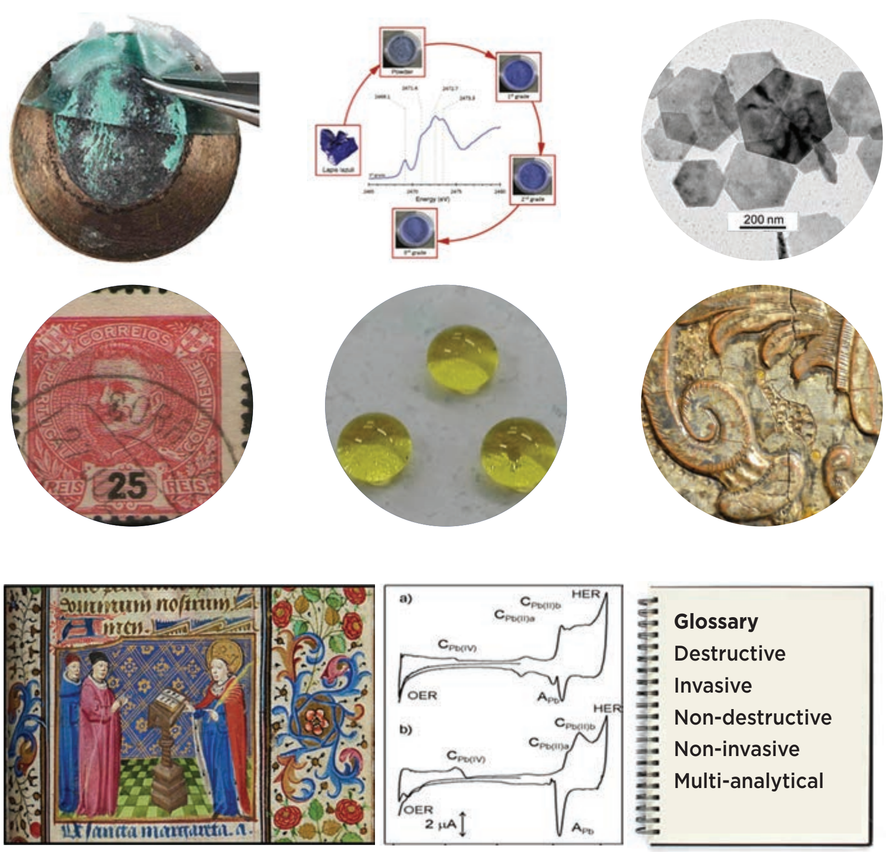
identification of minute samples can yield fundamental knowledge for conservation. Much of the knowledge of the materials of our past has been gained through microscopy and micro-analytical techniques which continue to dominate studies of works of art and cultural heritage. Increasingly sophisticated micro-analysis can be achieved by combining different methods for thorough study of the stratigraphy or samples, the oxidation state of elements, and micro-pore structure, for example.

One of the critical aspects of the study of cultural heritage, whether through analysis of micro-samples, or the use of micro-analytical techniques (either in situ or on the samples) is the relationship between a very small sample and the larger work of art which is intrinsically heterogeneous—and specifically if the sample is representative. To overcome this limitation, current use of in situ imaging techniques which can be low- cost, and in situ examination using suitable microscopy is fundamental prior to any sampling. Samples of works of art are unique—and techniques continue to develop for the study of materials; it is, therefore, likely that with advances in analytical science we will be better equipped to approach questions from conservators.

Pure and Applied Chemistry and Cultural Heritage

In a special issue of *Pure and Applied Chemistry* dedicated to Chemistry and Cultural Heritage, advanced analytical techniques are applied to characterize the materials and techniques used to produce artworks (spanning from ancient times to the twenty-first century), innovative methodologies are developed for cleaning and conservation, and degradation and change of art materials is studied [3].

Seixas de Melo and Pinto discuss the benefits of fluorescence emission in the UV-VIS for characterizing the dyes of the first Portuguese postage stamps. Antonio and Teresa Doménech-Carbó, authors of the book "Electrochemical methods applied to archaeometry, conservation and restoration" (2009), review the various applications of electroanalytical techniques in cultural heritage, covering 17 years of innovative contributions, and discuss exciting future developments in this area. Synchrotron based techniques provide unique insights into the complexity of materials, and by monitoring the sulfur XANES fingerprint, Monica Ganio *et al.* provide new clues for understanding the complex purification



In the PAC March 2018 special issue advanced analytical techniques are applied to characterize the materials and techniques used to produce artworks (spanning from ancient times to the twenty-first century), innovative methodologies are developed for cleaning and conservation, and degradation and change of art materials is studied. A glossary is provided at https://doi.org/10.1515/pac-2018-0106.

of lapis lazuli reported in many medieval treatises; lapis lazuli blue was an important color in medieval times. Ganio also shows that radiation damage is observed during the first steps of irradiation. Testing the threshold for sample damage caused during analysis using XANES is extremely relevant for the cultural heritage community. Nati Salvadó and her group provide the perfect example of the use of complementary analytical techniques. Colored translucent glazes over gilding in Baroque altarpieces (1671–1775) from the cathedral of Tortosa (Catalonia) were studied with synchrotron based ì-XRD and ì-IR and SEM-EDS, without altering their original layered microstructure. This approach enabled the assessment of the degradation resulting from the interaction among the compounds present in different layers. Hyperspectral imaging is another hot topic covered in this special issue; Marc Walton et al. discuss how to improve the quality of the data handled without being overwhelmed by the enormous datasets acquired.

Cleaning of bronze outdoor sculptures is the challenge addressed by Rodorico Giorgi *et al.*; cleaning is a crucial intervention as it is extremely difficult to accurately assess "what should be removed from an object". Italy is a country well-known for interminable disputes on the effect of cleaning interventions, centered on the question "was the original layer left by the artist removed or not?" One of the most famous disputes was the cleaning of Michelangelo wall paintings in the Sistine Chapel in Rome. Giorgi and his team provide a perfect example on how to address the challenging cleaning of outdoor metal sculptures; first, sound evidence on the molecular degradation mechanism is provided, which enables the characterization of the main degradation products and their multilayer structure. Film forming PVA-based cleaning systems are then used for the removal of corrosion products from historical bronzes; their safeness and efficacy is assessed in artificially aged mock-ups and, finally, applied in the cleaning of "Fontana dei Mostri Marini" by Pietro Tacca in Florence.

Nanomaterials have provided a breakthrough for conservation and restoration practice; examples of their efficiency are astonishing and call for a systematic assessment of their long-term molecular interactions with the original materials. Lime water, a saturated solution of $Ca(OH)_2$, has been used for centuries to consolidate carbonate-based substrates such as limestone or marble. Its importance as a protective and consolidant material for monumental surfaces is revisited by Carlos Rodriguez-Navarro *et al*. Developments of $Ca(OH)_2$ based formulations to overcome the limitations of the lime water treatment are presented and safer greener treatments are anticipated. Other innovative bio-inspired treatments for monumental surfaces are described by Maria J. Mosquera, Luis A.M. Carrascosa and Nabil Badreldin. Superhydrophobic properties as displayed by the lotus leaf combine self-protection and self-cleaning capabilities. The authors show how promising superhydrophobic/oleophobic coatings may be for the preservation of cultural heritage building materials.

References

1. B. G. Brunetti, A. Sgamellotti, A. J. Clark. *Acc. Chem. Res.* **43**:693 (2010).
2. P. Baglioni, E. Carretti, D. Chelazzi. *Nat. Nanotechnol.* **10**: 287 (2015).
3. J. Wouters. *Chemistry International* **30**(1), 4-7 (2008); https://doi.org/10.1515/ci.2008.30.1.4

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IUPAC, analytical chemistry and our cultural heritage†

by *D. Brynn Hibbert*

Considering the explanation of "Who we are" on the web site of IUPAC [1] I think the following is relevant to the theme of this special edition. "We are a leader in the provision of objective scientific expertise for the resolution of critical global issues that involve every aspect of chemistry, all of which have societal impact". The cultural heritage of the world belongs to the world, and a world body, such as IUPAC, is needed to provide the intercontinental [2] understanding that allows open science and sharing of approaches to conserving our important artefacts.

Professor Melo and colleagues writing the preface to the papers in this issue quote Louis Pasteur "(...) *il n'est pas possible de bien conserver ce que l'on connait mal*". Not being able to conserve what we do not know echoes the wider motto of many National

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