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GUEST EDITORIAL

Advanced Techniques in Art Conservation

It is well-known that historical artifacts and works of art deteriorate because of physical and chemical interactions with the surrounding environment. These processes can be thermodynamically and kinetically complex and can lead to discoloration, structural weakening, corrosion, and other alterations that, in the absence of intervention to stop or slow degradation, may result in a myriad of negative consequences, ranging from the incorrect "reading" of a work of art to its complete loss. It follows that detailed knowledge of the composition and structure of the materials used by artists, to include the behavioral properties of these materials, must be a fundamental component of successful and durable conservation and restoration methods.

Current scientific research is making appropriate contributions to the conservation of artistic heritage though projects that, for the most part, are dedicated to the improvement of analytical techniques for diagnostic assessment, the identification of the causes and effects of deterioration processes, and the development of new methods of effective and secure restoration. Such research is especially challenging owing to the fact that historical objects are unique and irreplaceable, which demands that analytical investigation must be noninvasive or, at the very least, employ microsampling techniques. In addition, conservation treatments must be completely reversible or executed with materials and methods compatible with the original object.

This special issue of *Accounts of Chemical Research* owes its genesis to Ivano Bertini, who brought together the guest editors at a meeting held in the quintessential city of art, Florence. The Accounts in this issue comprise a panorama of the most advanced ongoing research, yet, while offering as broad a view as possible, it cannot be comprehensive because of the extraordinarily wide range of materials encountered in art and the complicated way in which they have been used. The research activities described here focus on the development and deployment of advanced analytical methodologies and procedures, the characterization of the origin and mechanisms of material decay, and the creation and testing of new cleaning and consolidation treatments.

Today, a variety of analytical techniques are available that facilitate the investigation of the details of alteration processes, the identification of degradation mechanisms, and the discovery of the onset of decay. Owing to the advantages afforded by its high sensitivity, synchrotron radiation methods have been widely exploited in recent years. Among the available tools, X-ray absorption spectroscopy (XAS) offers a combination of features particularly well-suited for the study of art. Chemical mapping at high spatial resolution, for instance, provides information on the distribution of local phase composition and chemical states. XAS is used to reveal techniques of execution, to explain optical properties, and to visualize details of alteration reactions. Since synchrotron radiation techniques offer large depth of focus and fast acquisition, time-resolved measurements are also possible in customized sample environments, as in the study of corrosion processes in metals as they occur.

One research trend focuses on the development of methods for the subsurface investigation of objects without recourse to invasive transversal cross sections. X-ray based tomography and laminography have been exploited to explore in three-dimensions the inner, multilayered structure of paintings, demonstrating the possibility of examining the in-depth structure, the state of conservation, and the technology of manufacture of other types of objects. Terahertz time-domain spectroscopy has been shown to be capable of highlighting interfaces in a stratigraphic structure, while macroscopic-scanning X-ray fluorescence has been used to uncover the subsurface distribution of pigments. Optical coherence tomography exemplifies an appropriate noncontact method of optically sectioning partially transparent objects, with a resolution in the micrometer axial range.

Stray-field nuclear magnetic resonance (NMR) also offers opportunities for research innovation and noncontact subsurface investigations. Small portable stray-field sensors for NMR relaxation measurements have been developed that have a penetration depth of a few millimeters in a variety of materials and a resolution of a few micrometers. Multiband IR imaging permits better visualization of underdrawings, as well as the distribution of materials in paintings, by means of the processing of multispectral images as pixel by pixel subtraction and ratio or as false color representations.

Because works of art are especially vulnerable to degradation, the chemical characterization of their organic natural materials is of primary importance. The many significant advances made in the strategies and procedures employed in gas chromatography−mass spectrometry (GC-MS) have greatly improved the ability to distin-

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guish complex mixtures in degraded small samples. Of particular interest is the problem of determining the distribution of organic materials in cross sections of paintings or alteration layers. Secondary ion mass spectrometry (SIMS) and combined Fourier transform infrared and Raman (FT-IR/Raman) microspectroscopy techniques, including mapping and imaging, are suitable for these purposes. To obtain specific refinements in the identification of proteins, immunofluorescent probes can be used to detect targeted molecules with high sensitivity and specificity.

Traditionally the identification of dyes has required relatively large samples in order to be analyzed by high-performance liquid chromatography (HPLC). Recently, successful efforts have been made to identify dyes from samples as small as a few tens of micrometers in diameter exploiting surface-enhanced Raman spectroscopy (SERS). A noninvasive approach to the study of dyes in art is possible using UV−vis fluorescence-based analysis. Macro- and microfluorimetry offer the great advantages of being noninvasive as well as highly sensitive, despite having the disadvantage of the lack of molecular fingerprints as disclosed by vibrational spectra. This limitation may be overcome, however, using pertinent databases compiled from measurements taken on accurate reproductions of historical dyes.

Among the approaches discussed here, theoretical calculations also play a significant role. They permit the structural, electronic, and spectroscopic properties of materials to be modeled for spectral assignment or modeling of the kinetics of chemical processes in a changing environment, in order to simulate degradation phenomena.

At present, considerable efforts are also under way to develop portable instrumentation for noninvasive analyses to be carried out on-site, where the object is located or exhibited. Taking the laboratory to the art, rather than vice versa, reduces the risks and costs associated with the transportation of precious and delicate objects to the lab and opens the way to the scientific examination of a great many works of art. The noninvasive approach allows chemists to carry out multitechnique noncontact analyses on a virtually unlimited number of points and in many cases obtain a more thorough description than is possible with a limited number of specimens.

Such advanced techniques have answered many questions about the analysis and weathering of glass, as well as elucidating key points about the mechanisms responsible for damage to stone induced by in-pore crystallization. As a result, new methods of treatment are being proposed that offer the possibility of attacking the actual cause of the problem, rather than merely treating the symptoms. Other advances relevant to conservation concern studies of microstructure and color-formation processes in stoneware, and the use of ancient hybrid materials (inorganic and organic) in ancient buildings. Recent studies have been carried out as well on materials and painting methods used in the production of Byzantine icons. These studies not only allow the objects to be placed in their proper historical and cultural framework but also lead to the development of suitable long-term conservation strategies.

In the field of restoration intervention, today nanotechnology allows restorers to provide innovative cleaning and consolidation methods, such as those that utilize water-based micelles, microemulsions, or calcium hydroxide nanoparticles. The methods are both effective and fully respectful of the physicochemical properties of the original materials used by the artist. Substantial improvement in restoration is also afforded by the synthesis of innovative gels that are easily removed from the painting surface after cleaning, owing to the fact that they are rheoreversible or nonadhesive or because they contain magnetic-coated ferrite nanoparticles.

Laser ablation, too, has a very important role among innovative cleaning methodologies, since it offers the advantages of high control, accuracy, material selectivity, and immediate feedback. Prior to its application, it is imperative to test the effectiveness and gradualness of the ablation by means of choosing the appropriate pulse duration, maximizing the selectivity, and minimizing the risk of photothermal and photomechanical effects. In this regard, the potential use of femtosecond pulse lasers to overcome the limitations of nanosecond ablation methods has been recently explored.

The entirety of the work reported in this special issue clearly shows how, today, chemical research concerning the study and conservation of art is a very active and productive field. The advances of recent years can be attributed to the enormous progress made in the development of analytical technologies, as well as to the widespread and increased attention given by the public and by policy-makers to the preservation and enhancement of the historical heritage of all nations. The worldwide realization of the social and economic value of the conservation of our heritage, as well as the rapid invention of new technologies, will surely generate exciting perspectives for future research.

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