ACCOUNTS
of chemical research

Synchrotron-Based X-ray Absorption Spectroscopy for Art Conservation: Looking Back and Looking Forward

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RECEIVED ON JULY 11, 2009

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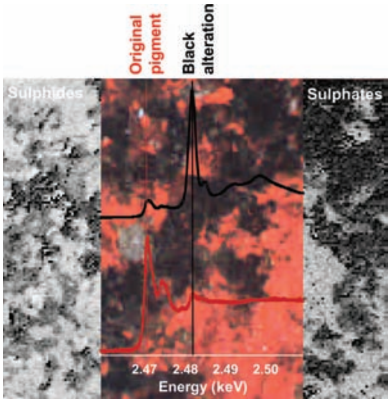

A variety of analytical techniques augmented by the use of synchrotron radiation (SR), such as X-ray fluorescence (SR-XRF) and X-ray diffraction (SR-XRD), are now readily available, and they differ little, conceptually, from their common laboratory counterparts. Because of numerous advantages afforded by SR-based techniques over benchtop versions, however, SR methods have become popular with archaeologists, art historians, curators, and other researchers in the field of cultural heritage (CH). Although the CH community now commonly uses both SR-XRF and SR-XRD, the use of synchrotron-based X-ray absorption spectroscopy (SR-XAS) techniques remains marginal, mostly because CH specialists rarely interact with SR physicists. In this Account, we examine the basic principles and capabilities of XAS techniques in art preservation.

XAS techniques offer a combination of features particularly well-suited for the chemical analysis of works of art. The methods are noninvasive, have low detection limits, afford high lateral resolution, and provide exceptional chemical sensitivity. These characteristics are highly desirable for the chemical characterization of precious, heterogeneous, and complex materials. In particular, the chemical mapping capability, with high spatial resolution that provides information about local composition and chemical states, even for trace elements, is a unique asset.

The chemistry involved in both the object's history (that is, during fabrication) and future (that is, during preservation and restoration treatments) can be addressed by XAS. On the one hand, many studies seek to explain optical effects occurring in historical glasses or ceramics by probing the molecular environment of relevant chromophores. Hence, XAS can provide insight into craft skills that were mastered years, decades, or centuries ago but were lost over the course of time. On the other hand, XAS can also be used to characterize unwanted reactions, which are then considered alteration phenomena and can dramatically alter the object's original visual properties. In such cases, the bulk elemental composition is usually unchanged. Hence, monitoring oxidation state (or, more generally, other chemical modifications) can be of great importance. Recent applications of XAS in art conservation are reviewed and new trends are discussed, highlighting the value (and future possibilities) of XAS, which remains, given its potential, underutilized in the CH community.

1. Introduction

Whatever the technical and methodological approaches, questions commonly tackled by archeologists, art historians, and curators can be broken down into two main categories, a better understanding of the past and a well-founded prediction of the future. As regards the past, analyses are intended to reveal the manufacturing

Published on the Web 01/08/2010 www.pubs.acs.org/acr
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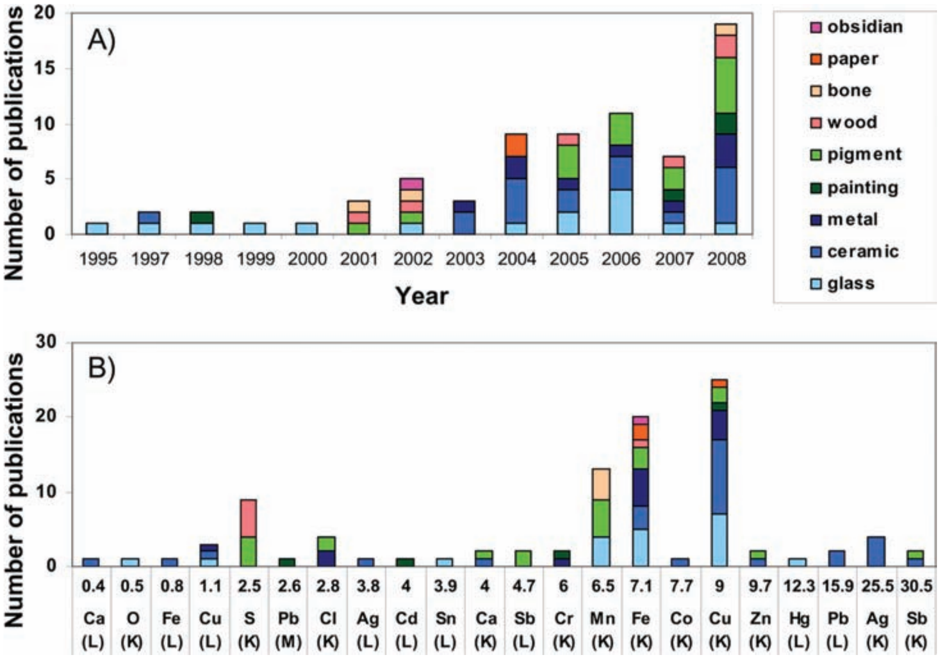

FIGURE 1. Evolution of the publications reporting XAS analyses on CH items over the past decade. Statistics are sorted by type of material (A) versus time and (B) versus elements and absorption edges.

secrets behind specific artifacts; choice of ingredients, manufacturing processes (extraction of the materials, purification, heat treatment, chemical synthesis, etc.), geographic provenance, and trade routes, as well as authentication, constitute the main information that art historians seek to uncover. Regarding the future, a great deal of research is being carried out to understand alteration phenomena in a more profound manner with the final goal of improving methods of restoration and conservation.

Various traditional analytical tools are used in laboratories to perform chemical analyses on museum objects. However, such chemical characterizations are challenging for many reasons. First, the artifacts are precious, so sampling is usually forbidden or at least limited in number and size. Second, works of art are often made of complex (organic/inorganic, crystallized/amorphous) heterogeneous, and multimaterial mixtures of simple compounds; hence high sensitivity and high lateral resolution can be advantageous.

Several synchrotron radiation (SR)-based analytical techniques are now available, such as X-ray fluorescence (XRF), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FTIR). They are not conceptually different from their widespread laboratory counterparts. However, the higher sensitivity, minimal sample preparation, and possibility of conducting analyses at the microscale (or submicroscale) provided by SR offers significant advantages over laboratory methods. A detailed review of such methods is beyond the scope of this Account. Here, we will focus mainly on the basic principles and capabilities of X-ray absorption spectroscopy (XAS) techniques.

The use of SR in Cultural Heritage (CH) applications was first mentioned in 1986 by Harbottle et al. who anticipated that SR-based techniques would "quickly take a prominent place in archaeometric research".[1] As a natural extension of conventional laboratory techniques, SR-XRF and SR-XRD became rapidly popular in the CH community. Conversely, use of XAS remained marginal, mostly because of a lack of interaction between CH specialists and SR physicists.

However, underpinned by the dramatic improvement of both synchrotron sources and beamline instrumentation, XAS became increasingly used in archaeometry. Indeed, in addition to the above-mentioned advantages, XAS techniques are appealing because they can be equally applied on amorphous or crystalline materials. When combined with the XRF detection mode, XAS also benefits from low detection limits, thus permitting the analysis of both major and minor or even trace elements. Finally, it provides rather straightforward access to oxidation states and more generally to chemical speciation information.

As shown in Figure 1A, the applications of XAS cover an array of materials, ranging from hard matter such as glass, ceramics, and metal to softer materials such as paintings, bone, wood, or paper. In the current context, historical knowledge and art conservation studies rely on similar chemical

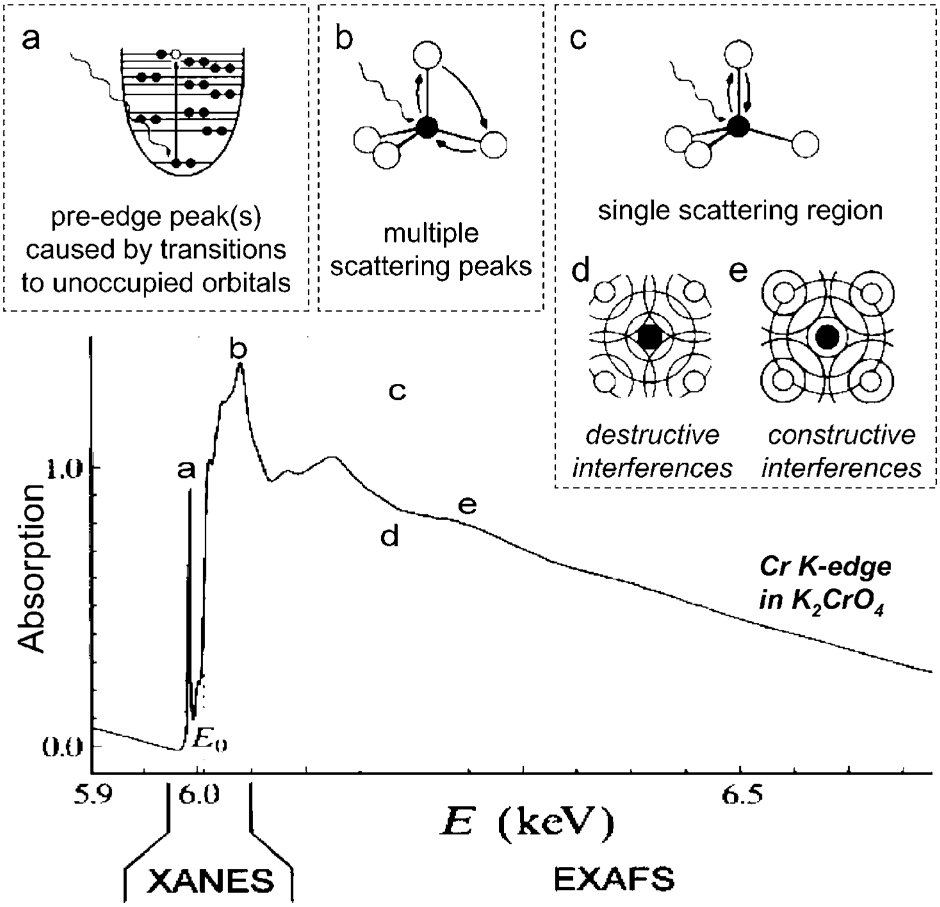

FIGURE 2. Principles of XAS.

characterization methods for both groups of materials. However, they differ in their scientific scope: The main objective for the first group of materials is to understand their original fabrication process. This mostly concerns the craftsman's control over synthetic reactions at high temperature resulting in various optical effects in glasses, glazes, lusters, ceramics, and pigments. Studies on the second group of materials focus on unintentional degradation reactions. In general, these occur over longer time scales and are either due to past conservation treatments or due to passive external circumstances or may even be inherent to the chemical compounding of the artwork itself. Both types of studies will be illustrated by different examples.

2. Basics of X-ray Absorption Spectroscopy

XAS techniques are based on the measurement of the variation in the absorption coefficient while scanning the energy of the probing X-rays photons in a narrow region around an absorption edge (Figure 2). This variation is physically related to the excitation cross section of the core electrons into unoccupied electronic states or into the vacuum continuum. The spectral features observed close to the absorption edge, referred to as the X-ray absorption near edge structure (XANES), reflect the molecular environment (oxidation state, coordination numbers, site symmetry, and distortion) of a given absorbing atom and provide the basic mechanism for imaging with chemical specificity.[2] Information on different electronic states within systems that have the same elemental composition is therefore possible. A similar method is also used in electron microscopes by performing electron energy loss spectroscopy (EELS). However, the specificity of the interactions of X-rays with matter offers some advantages to XANES over EELS microscopy: micro-XANES has been proven to have a better spectral sensitivity, to produce less radiation damage, and to benefit from a larger penetration depth for bulk analysis.[3]

Extended X-ray absorption fine structure (EXAFS) is measured when the energy of the incoming X-rays is scanned far beyond the absorption edge of interest. EXAFS oscillations result from constructive and destructive interference between the outgoing and backscattered photoelectron waves. The physical processes giving rise to the EXAFS signal are generally well-understood and can be modeled using appropriate computer programs, which make it possible to assess, with

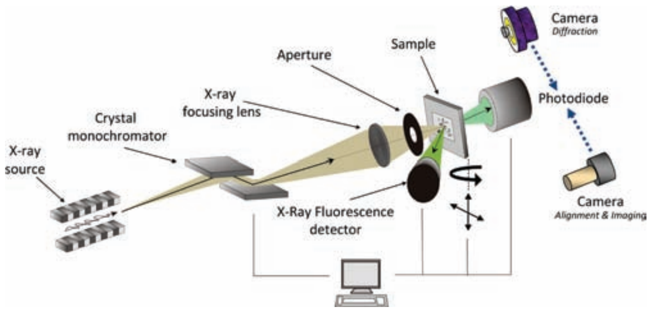

FIGURE 3. Sketch of a state-of-the-art hard X-ray microprobe on SR beamline. Several detectors allow a multimodal approach by simultaneous signal recording.

reasonable accuracy, the identity of the surrounding atoms, specific bond distances, and coordination numbers.[4]

As a result of the removal of core electrons due to the X-ray absorption processes described above, atom de-excitation leads to the emission of characteristic "secondary" X-rays. These X-ray fluorescence signals permit elemental identification, mapping, and often quantification of the elements present in a sample in a similar fashion as can be done with nonsynchrotron techniques such as scanning electron microscopy (SEM)—energy-dispersive X-ray analysis (EDXA) and particle-induced X-ray emission (PIXE). The advantage of SR-XRF lies in its sensitivity, due to the high photon flux available, the large production cross section for XRF signals, the possibility of tuning energy, and the low scattering cross sections. Quantification is comparatively straightforward because the physics of photon interaction with matter is relatively simple and well-understood. As discussed above, the absorption edge of an element is related to the chemical environment of the absorbing atom and its oxidation state. Therefore, by selecting appropriate energies of the incoming X-ray photon, it is possible to generate chemical maps of an element in relation to its oxidation state and chemical bonding.

As depicted in Figure 3, the most advanced hard X-ray microprobes usually offer a multimodal analysis platform where SR-XRF, SR-XAS, and SR-XRD can be combined. The sample is usually raster scanned, and data are collected at each pixel to generate corresponding elemental, structural, or chemical maps. Most SR-XRF instruments rely upon a specific 45°/45° geometry where the sample is canted 45° to the incident beam and X-ray detectors are placed in the plane of the storage ring at $\sim$90° to the incident beam. With the incoming beam being naturally polarized in the horizontal plane, this geometry minimizes the contribution of scattered primary X-rays. Furthermore, the full control of both tunability and spectral bandwidth of the incoming monochromatic radiation minimizes radiation exposure without compromising the signal-to-noise and allows quantification with an accuracy of 3−5%.[5]

Most of the synchrotron set-ups can accommodate samples of different dimensions, and when using hard X-rays, they operate at atmospheric pressure. Therefore it is possible to perform local analyses on whole CH objects, as was done on Etruscan glass vessels and beads[6] or Van Gogh paintings.[7] However, today these examples remain marginal, mainly because of logistic limitations (historical value, insurance cover, travel range/physical size of scanning stages, etc.). In this respect, sampling is often favored not only because it simplifies sample handling but also because it can give access to cross-sectional information.

It is noteworthy that "noninvasive analysis" does not always imply "nondestructive analysis" because X-ray irradiation may result (to some degree) in radiation damage. In addition to a possible local blackening (limited to the size of the probe), more subtle chemical changes due to photoreduction have been reported in cases of hybrid or organic materials such as iron gall ink[8,9] and blood-containing African patinas.[10] This photochemical effect usually decreases the oxidation state of the targeted element. Being directly proportional to the photon density, this process can occur very rapidly, in the range of a few minutes, when using a submicrometer probe. If underestimated, this artifact can lead to misleading conclusions and should be systematically addressed. Indeed, this problem is far from being specific to CH samples, and several ongoing developments on high-efficiency detectors aim to minimize time exposure and consequently the total absorbed dose at each examined position.

3. Historical Knowledge and Ancient Manufacturing Technologies

XAS techniques were first applied to ancient glasses[11,12] (Figure 1A,B). More recently, glazes and ceramics, based on similar vitreous matrices, have also benefitted from an increasing interest. Indeed, XAS techniques are particularly adapted for the study of these types of materials. Combined with the good match between method capabilities (short-range probe, sensitive) and material properties (amorphous and diluted state), XANES and EXAFS provide unique chemical information. Historical vitreous materials were highly valued because of their optical properties. The interplay between transparency, opacity, color, metallic shine, colored iridescence, and other properties are still appealing today but must have been highly appreciated in the object's contemporary times. Such effects can be induced by the presence of opacifying crystals, ionic chromophores, or metallic nanoparticles as well. The oxidation state of elements and more generally their chemical environment within the vitreous matrix is directly correlated to these optical effects. The historical production method therefore required adequate control of firing conditions (temperature, atmosphere, and time), as well as the introduction of oxidizing or reducing ingredients.

Coloring variations are usually obtained in glass by modulating the oxidation states of transition elements such as Mn, Fe, Co, and Cu; these elements have characteristic absorption frequencies in the visible region as a result of d−d electronic transitions.[11] This explains the high number of XAS studies at the K-edge of these elements (Figure 1B). For instance, XANES analyses of ancient glasses from the Patti roman villa (Messina, Sicily) at the Fe and Mn K-edges supported the hypothesis that pyrolusite (MnO_2) could have been added intentionally as a decolorant during the melting procedure.[13] However, many of the above-mentioned optical effects (such as transparency) can be affected by long-term corrosion. For instance, the oxidation of Mn^{2+} into Mn^{4+} has been observed in medieval glass windows exposed to progressive weathering in Cathedral du Bosc, Normandy, France, (14th Century).[14] This oxidation results in the precipitation of manganese oxi-hydroxides, which in turn lead to opacification and a change in color (brown) of the glass panes.

In the case of lusters, the skills of many craftsmen were honed toward producing a metallic shine and a colored iridescence on the surface of ceramic objects. These optical properties result from the presence of an inhomogeneous dispersion of metallic (usually silver or copper) nanoparticles in the first outermost micrometer of the glaze. Following pioneering transmission electron microscopy studies, a number of projects dedicated to luster characterization by EXAFS and XANES were initiated aiming mainly at establishing a correlation between color (red, gold, or green), chemical composition, and copper or silver oxidation states.[15,16]

Beyond the family of vitreous-based artworks, XAS techniques can also be exploited to track possible heat-induced color transformations in various pigments. This has proven to be particularly relevant for manganese-based pigments. For instance, Mn K-edge XANES and EXAFS were used to understand the thermal effect on the structural environment of Mn in fossilized mastodon ivory or bone. The heat-induced oxidation of $Mn^{2+/3+/4+}$ into Mn^{5+} and further substitution for P^{5+} in the apatite matrix is responsible for the blue rendering of these pigments, usually called odontolite, or bone turquoise, since it perfectly imitates the color of mineral turquoise.[17]

In a different context, Mn XANES was employed for the characterization of black pigments found in Spanish and French prehistoric caves. Several atypical manganese oxide minerals such as manganite, groutite, todorokite, and birnessite were identified. TEM and XANES analyses revealed that, instead of synthesizing these compounds through heat-induced reactions, natural pigments were favored. Thus, these raw pigments, rare in nature, are likely to originate from nonlocal geological sites and may have had to be imported from a distant location.[14,18]

4. Alteration, Restoration and Preservation

Most of the alteration processes, for example, metal corrosion, involve modification of the redox states of the original material, while the average elemental composition of the bulk material remains unchanged. Alteration is then limited to a highly superficial surface gradient, which may have a thickness in the micrometer or even submicrometer range. Yet, such pure surface changes can have effects on the objects visual appearance. Probing the oxidation of specific elements, and more generally their chemical environments, is therefore of prime importance when studying alteration mechanisms. Degradations may be detected with greater significance with XAS than the change in the macroscopic, visual appearance of the object would suggest as reported, for instance, in the study of degradation of cadmium pigment.[19] While the conservators of the painting noted a slight discoloration of the yellow paint, the degradation layer itself could be better identified by XAS.

Metal corrosion is a major concern in art conservation.[20] XAS offers a direct observation (either as point, profile, or map acquisition) of metal speciation. Such measurements have mainly been performed on iron[21] or bronze[22,23] artifacts. In all of these works, mention is made of the interest of combining several microanalytical techniques such as SEM-EDX, XRF, XRD, Raman, and XAS. The XRF/XAS combination is rather natural as all the XRF emission lines below the XANES edge being investigated are recorded simultaneously. For instance, Reguer et al. demonstrated a clear correlation between the iron valence distribution in multilayered corrosion products and the evolution of chloride concentrations.[21]

XAS techniques are also increasingly used to study chemical reactions involved during pigment alteration processes. As an example, sulfur-based pigments, such as HgS (cinnabar when natural, vermilion when synthetic), as well as CdS, may suffer from discolorations. While red HgS tends toward shades of gray or black, bright yellow CdS may evolve into a white

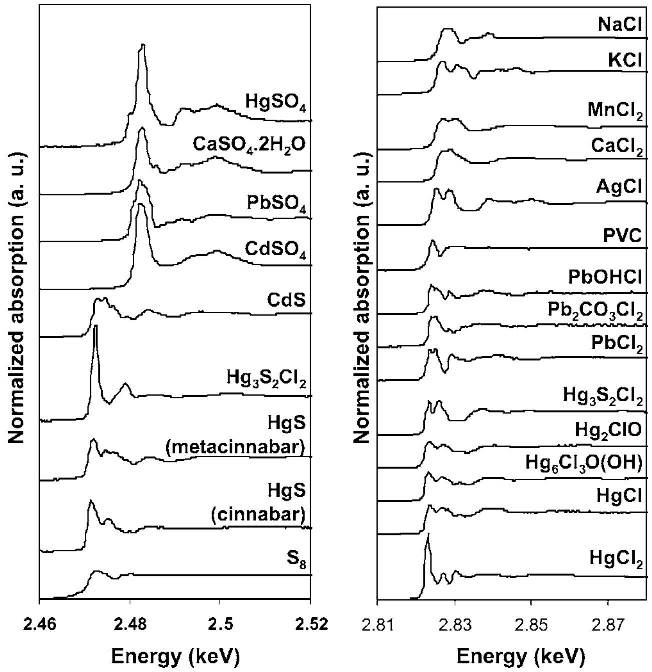

FIGURE 4. Examples of XANES spectra (K-edge) of sulfur (left) and chlorine compounds (right) occurring in art materials.

transparent matter. XANES at the sulfur K-edge revealed that both HgS, in Pompeian paintings,[24] and CdS, in paintings by the 19th Century artist James Ensor,[19] are subject to oxidation. The XANES features probe the sulfur oxidation states directly (Figure 4) and can be used straightforwardly to map the different sulfur species.

Besides sulfur oxidation, chlorine was identified as an additional potential player in cinnabar degradation. In some Pompeian paintings,[24] as well as Gothic paintings from Pedralbes, Barcelona[25] (Figure 5), XANES revealed the formation of mercury—chloride chemical bonds, specifically in gray-altered regions. Interestingly, the presence of the element chlorine was not systematically related to alteration. It was, for example, observed as the nonreactive pollutant NaCl on a surface of a red Pompeian painting.[24] Chlorine XANES spectra exhibit features that make it possible to distinguish mercury chloride compounds from alkaline and alkaline earth chlorides (Figure 4). Thus it was possible to selectively map the distribution of mercury chloride compounds in cross sections of a Gothic painting, showing the blackening of cinnabar (Figure 5). This figure shows that mercury chloride compounds are limited to the gray region, on top of the cinnabar layer, while other chlorides, presumably $CaCl_2$, are present beneath the pigment (in the mortar).

More generally, chlorine is frequently involved in artwork degradation, either in paint layers, metals, or glass. It can affect not only materials previously immersed in salt water but also artifacts that are kept in the vicinity of the sea. Furthermore, chlorinated cinnabars have already been reported in paintings stored in museums, such as London National Gallery[26] (Raman analyses) and the Louvre[27] (XANES analyses). Accordingly, XANES at the Cl K-edge will certainly find many future applications in art conservation, as complementary methods to laboratory analyses.

It is noteworthy that significant aesthetic damage is not necessarily associated with alterations throughout the bulk of the material and are limited to the objects outmost superficial layer. As observed in the previous examples, pigment alteration can be limited to the few outmost micrometers of the painting. Therefore, the characterization of such phenomena is challenging because the material (often the original pigment) present underneath the alteration can significantly contribute to the chemical signal detected. Submicrometer probes are particularly well-suited to the study of transversal cross sections, because they usually enable a discriminative analysis of both safe and altered regions.

A multiscale approach is equally important as exemplified in various studies that combine in-plane millimetric analysis over large painting surfaces with in-depth micrometric analysis of transversal polished sections.[7,24]

It should be pointed out that spatial resolution is determined not only by lateral resolution but also by penetration depth. This aspect clearly discriminates X-ray microscopy from electron microscopy. It can be an inconvenience as well an asset. Different strategies can be used to restrict the volume analyzed by the X-ray methods (see below, current trends). Conversely, the relatively high penetration depth of X-rays (in particular at high energy) can be fully exploited for 3D imaging.[28] At low energies, probe depth is limited by self-absorption. For instance, in HgS, 80% of the sulfur fluorescence lines are reabsorbed within the first 0.5 μm layer.

XAS analyses are also employed to gain a better understanding of the alteration of soft materials such as wood or paper. Indeed, these reactions can be affected by surrounding metallic compounds (such as iron bolts in wooden war ships or iron-gall ink in paper), which can act as catalysts in oxidation processes. For example, measurements of the oxidation state of iron can be used to characterize ink diffusion in paper and related chemical reactions leading to the disintegration of ancient manuscripts.[8,9,29]

Similar to painting characterization, a dual macro-/microstrategy was followed by Sandstrom et al. while studying marine wood degradation in two major historical war ships, the Mary Rose and the Vasa. Series of wood fragments were sampled at different depths, starting from the surface and cov-

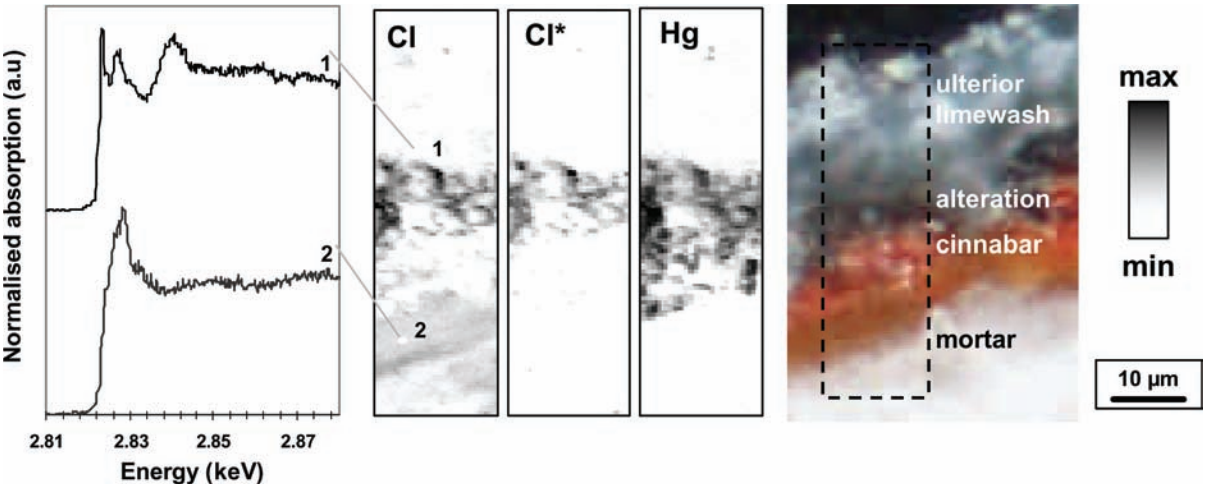

FIGURE 5. XANES spectra and chemical mapping of a blackening cinnabar from Pedralbes monastery.[25] Optical light microscope picture of the multilayer structure and regions of interest. Two chlorine XRF mappings, recorded with two peculiar energies of the incoming beam, 2.8231 keV, specific to Hg−Cl bonding (noted as Cl*), and 2.85 keV, which excite unselectively all chlorine species (noted as Cl).

ering several centimeters. Samples were then ground to powder and analyzed with a large beam in order to obtain an average measure of the sulfur oxidation states within the wood. Meanwhile, thin transverse wood sections were studied with a microprobe to gain information on the subcellular distribution of reduced sulfur within the individual cells of the wood.[30]

5. Current Trends

Recent methodological developments aim at pushing classical XAS experiments toward better control of additional experimental parameters, such as time or probing depth, or by combining XAS with other analytical techniques.

Toward Time Resolution. Alteration mechanisms, as for any chemical reaction, must be ultimately addressed as kinetic processes. The specific nature of works of art causes the time scale of these processes to be rather broad, ranging from hours to centuries. An additional degree of complexity is the multifactor character of the alterations, which are determined not only by environmental conditions and their variations but also by the intrinsic composition of the object. Reproducing such chemical reactions in the laboratory, with or without artificial aging, can be particularly rewarding for conservation purposes. Such studies attempt to understand alteration phenomena, while assessing the effects and the efficiency of conservation and restoration treatments. When such model processes are performed, physical and chemical conditions must be carefully monitored, from near-reality to extreme conditions.

In this context, SR techniques offer two main advantages: the large depth of focus, which allows scientists to use customized sample environments (electrochemical cells, furnace, etc.) during experiments, and the high flux, permitting fast data acquisition, which is essential for precise observation of the very first reaction stages. As an example, Adriaens et al. developed an electrochemical cell dedicated to the *in situ* monitoring of metal corrosion in marine conditions. Time-resolved XAS and XRD were used to monitor copper corrosion at the surface−solution interface in a sodium sesquicarbonate solution and to evaluate the effectiveness of protective coatings of lead objects.[31]

Similarly, *in situ* temperature monitoring is relevant for a better understanding of manufacturing processes of various artworks (glass, ceramics, lusters, etc.). Although several experiments combining off-line heat treatment and XAS measurements have been reported, such as on different manganese-based pigments,[17,18] online temperature-resolved experiments are still underexploited and so far have only involved XRD analyses. Pradel et al. studied high temperature reactions in model luster paint.[32] The authors could correlate the decomposition of metacinnabar and the subsequent creation of a sulfo-reducing atmosphere with the reduction of Cu^{2+}-containing compounds to Cu^{+}; an intermediate chemical state that leads to the formation of metallic Cu nanoparticles.

Toward in-Depth Resolution. Another trend consists in developing methods to tune the probed depth in order to obtain "in-depth" information without invasive transversal cross sections. Penetration depth can be tweaked by tuning the energy of the excitation photon beam. Gliozzo et al. measured the XANES spectra of Fe at both K- and L-edges on black gloss pottery from Northern Etruria to explain visual differences among different samples.[33] To probe the gloss at different depths, the authors relied on the difference in beam penetration between two energies, 7.1 keV (Fe K-edge) and 0.7 keV (Fe L-edges). Despite more complex experimental conditions (lower fluorescence yield, experiments in vacuum to prevent air absorption), XANES at the L-edges, with a penetration depth of about 0.1 μm, was essential to selectively probe the surface of the gloss. These low-energy acquisitions revealed a direct correlation between the Fe oxidation state and the visual appearance of the gloss.

Working at several edges of the same element usually requires distinct experiments, and often, as in the above example, on two different instruments. Conversely, other strategies rely on multidetection systems capable of simultaneous measurements at two different depths. Cartechini et al. performed XAS analysis on a XV^th^ century Italian painting to better understand copper resinate blackening and to establish a correlation between the color and the chemical environment of copper.[34] XAS measurements were conducted both in X-ray fluorescence yield mode (XFY) and in total electron yield mode (TEY) based on the collection of secondary electrons emitted. While XFY probes the first tens of micrometers, TEY accesses only the first few hundred nanometers at the surface of the paint layer. In this example, the strong analogy of spectral features in both modes led to the assumption that the copper local environment did not change across the depth of the blackened layer.

Similar to the combination XFY/TEY, combining XAS with optically detected X-ray absorption spectroscopy (ODXAS) offers identical modulation of probed depth. ODXAS relies on the measurements of near-optical photons (i.e., with wavelengths in the 200−1000 nm range), generated by secondary fluorescence processes. This method was exploited to perform high-resolution analysis of copper corrosion.[35] Model corrosion systems deposited on a copper substrate were analyzed in air and in a sodium sesquicarbonate solution, simulating typical conservation methods for copper-based objects recovered from marine environments. In such a configuration, the ODXAS is significantly more surface specific by probing the first 0.5−1.5 μm layer, while the XRF data are dominated by signals originating from the substrate. A similar ODXAS experiment was reported by Roqué et al. on the study of model lusters (metallic copper nanoparticles embedded in a glass matrix). The objective was primarily to correlate optical luminescence properties with chemical composition of metallic nanoparticles.[36]

Finally, the use of polycapillary-based set-ups provides a more versatile control of in-depth measurements. The so-called confocal geometry is based on the use of two X-ray lenses. One lens is used to focus the incoming beam while the second restricts the XRF detector angular acceptance to a small volume. The intersection volume of the incoming microbeam and the coinciding focus of the second lens determines the voxel size.[37] Such strategy has already been employed for depth-selective elemental analyses.[38] Extension to XAS studies is possible as well but is yet to find applications in the cultural heritage field.

Toward Multimodal Microspectroscopy. Combining XAS with other methods, in particular spectroscopic methods, is another way of enhancing the method. Beyond XRF, which is a natural and indeed essential companion method to XAS, vibrational techniques can be coupled to XAS in a fruitful manner. Raman and FTIR spectroscopy are complementary to XAS as all these methods share several characteristics: They all probe molecular groups while being quasi-noninvasive, can be used on similar samples, and can all generate medium- to high-resolution chemical maps.

While XAS is element-specific, vibrational spectroscopies simultaneously access a large number of molecular groups. Consequently, XAS is more sensitive and more adapted to the study of a single element of interest, whereas FTIR and Raman microscopy provide a global picture of the overall molecular composition. Such a combination can be performed off-line, as was done on paintings[34] or on patina sampled from African statues.[10] The new potential of combining vibrational and electronic microspectroscopies is increasingly addressed on various facilities.[3]

6. Conclusions

As already stated by Nakai et al. in 1997,[11] XAS techniques are particularly relevant for the analysis of artifacts. Experiments can be performed in air, directly onto the entire object, without any sample preparation. Conversely, focusing the beam down to submicrometric size enables precise and selective mapping. Analyses can be carried out on any kind of material (from hard to soft), in particular on vitreous matrices. They can also be applied to many elements, as opposed to Mössbauer spectroscopy, which is limited to a small number of elements.[39] When XAS spectra are acquired in XRF detection mode, the sensitivity is very high. Thus, minor or trace elements, which may have major impacts on the appearance of works of art (e.g., chromophoric elements in glass or chlorine in paintings) can be probed. Similarly, the chemical sensitivity provided by XANES and EXAFS is very high and offered particularly significant information in many cases. On the one hand, many analyses are carried out to study historical production techniques used to create appealing visual effects in vitreous materials. This includes color, translucence, opacity, iridescence, etc. in glasses and ceramics. Many of these effects result from electronic transitions that are directly related to the chemical/electronic state of some transition metals. On the other hand, phenomena of unintentional, postproduction degradation are often directly connected with modification of the molecular surroundings (change of the oxidation state, reaction with exogenous chemicals, etc.) of these metals. In both cases, obtaining information about the chemical environment of specific elements is highly relevant. Furthermore, combining high lateral resolution with high chemical sensitivity (resulting from SR high flux and energy tunability) provide an unrivaled way of generating chemical maps. Finally, the possibility of combining these various analytical features in a single experiment is one of the unique assets of these methods. After one or two decades of exploratory and demonstrative studies, SR-XAS and SR-XRF are now recognized as appropriate methods for tackling challenging questions in art conservation that cannot be addressed using conventional laboratory methods. Both the SR and CH communities are now aware of the advantages associated with this synergy and several partnerships are being built, as exemplified by the IPANEMA institute at the SOLEIL[40] synchrotron, as well as the creation of dedicated review panels in several other SR facilities. Finally, current technological developments such as time-resolved XAS measurements, the use of nanoprobes, and the possibility of performing ultrafast scans will undoubtedly open new avenues in the field of analytical chemistry applied to art conservation.

BIOGRAPHICAL INFORMATION

After gaining the "agrégation" of chemistry at the "Ecole Normale Supérieure" (Lyon), **Marine Cotte** obtained her Ph.D. for her research at the C2RMF on lead-based cosmetics and pharmaceutical compounds used in Antiquity. During her postdoctoral fellowship at the ESRF, she has expanded the application of X-ray and FTIR microspectroscopies to paintings. She has now a twofold position as a permanent CNRS scientist (C2RMF) and as a beamline scientist (ESRF).

Jean Susini obtained his Ph.D. in Chemical Physics at the University Pierre et Marie Curie (Paris) and joined the ESRF in 1989. In 1994, he took responsibility for the design, construction, and operation of the X-ray microscopy beamline. He led the ESRF X-ray Microscopy and Microanalysis Group and coordinated the operation and scientific program of several instruments, including hard and soft X-ray microprobes and the infrared spectromicroscopy station. In 2009, he was appointed Head of the Instrumentation Services and Development Division of the ESRF.

Joris Dik trained as art historian at the University of Amsterdam under the supervision of Prof. E. Van de Wetering and then obtained a Ph.D. in X-ray crystallography at the Free University of Amsterdam, focusing on the synthesis and alteration behavior of the pigment lead-tin yellow. His research interest is to apply novel methods of scientific investigation to art-history problems. He currently is associate professor at the Technical University of Delft, The Netherlands.

Koen Janssens obtained his Ph.D. in Analytical Chemistry from the University of Antwerp (Belgium) and became professor at this university in 2000. He has employed since 1990 intense beams of X-rays for nondestructive materials analysis, and he was, together with F. Adams and A. Rindby, editor of *Microscopy X-ray Fluorescence Analysis* (Wiley, 2000) and, together with R. Van Grieken, of the *Non-destructive microanalysis of Cultural Heritage materials* (Elsevier, 2004). His main fields of interest are X-ray based microanalysis of materials with special attention for local speciation of metals in (altered) environmental and cultural heritage materials such as glass and inorganic painters' pigments.

FOOTNOTES

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