SYNCHROTRON RADIATION
IN ART, ARCHAEOLOGY AND CULTURAL HERITAGE SCIENCE

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Abstract

The scientific investigations aimed to the study, characterization and conservation of archaeological and artistic finds are in general based on a strong interdisciplinary approach, which implies the collaboration among scientists and archaeologists expert in many different fields. The knowledge transfer between different research groups is in particular required by the considerable amount of different conventional and advanced techniques which can be applied to ancient materials. This requires that researchers have specific technical and scientific background.

One of the main requirement imposed by the archaeologists in the studies of ancient and precious materials is that the selected techniques must be non-destructive (or at most micro-destructive). In this scenario, synchrotron radiation-based methods can play a central role, being specifically suitable for micro-non-destructive analyses.

The objective of this lesson is to show how synchrotron radiation-based experiments, employing highly brilliant and collimated micro-beams of X-rays can be exploited in diffractometric, spectroscopic and imaging investigations of archaeological and artistic objects, obtaining results with unprecedented space and energy resolution.

Introduction

The application of synchrotron radiation (SR) in archaeological and cultural heritage (CH) science is relatively recent, dating to the end of '80s, and it became wide spread only in the last years, thanks to a more continuous dialog between archaeologists and experts of the physical and chemical techniques based on the use of SR and neutrons. This welcome development is mainly due to the fact that, for many reasons, SR is a very suitable and powerful tool in the investigations of very rare and fragile objects, on which no damages must be induced and only non-destructive analyses are allowed. Moreover, a peculiar characteristic of the archaeological finds is that they are often heterogeneous and complex in shape and composition (pottery, glass, metals, paper, pigments, wood, cloths, etc.). In addition, ancient materials are often covered by alteration layers. For all these reasons, the use of micro-beams and the analysis of micro-volumes of material is mandatory.

The main questions that archaeologists ask most often regarding an ancient object are:

1) what material is it made of (composition);
2) when was it made (dating);
3) where was it made (provenance);
4) how was it made (art technology);
5) how can we avoid its destruction (conservation).

To answer these questions, a thorough knowledge of the nature of the original materials and of the ancient production techniques is mandatory. At synchrotron laboratories, experiments based on highly brilliant and collimated micro-beams of X-rays are employed to obtain diffraction, spectroscopic and imaging data with unprecedented space and energy resolution.

The SR-based investigations more frequently performed in archaeometric studies are the following:

a) Elemental microanalysis down to the sub-ppm level, by means of X-ray fluorescence analysis (μ-XRF).

b) Local chemical state determinations of selected (trace) constituents, using XAFS and μ-XAFS (X-ray absorption spectroscopy)

c) Information on the presence and nature of crystalline phases, by means of X-ray diffraction (XRD), which usually employs X-ray photons with energies in the 0.5 to 30 keV range.

d) Entire objects may be bathed in highly-energetic synchrotron beams to allow high quality radiographic or tomographic imaging measurements, revealing the internal structure of these artifacts.

Here, some of the most common techniques will be discussed with the aim to highlight the essential role of SR in the resolution of several important archaeological problems.

Archaeometrical applications of synchrotron X-ray diffraction

X-ray diffraction, and in particular X-ray powder diffraction (XRPD), is a very frequently applied technique in Materials Science, even with conventional sources. XRD is the main experimental technique for probing the long range order of atoms and is the most straightforward method for identifying crystalline phases. When it is supported by the use of SR, it can provide excellent signal/noise ratio and excellent peak resolution and allows performing micro-diffractometric non-invasive investigations. Moreover, diffraction patterns contain information on the dimensions and arrangement of the microscopic grains, which is related to the technique used to produce the artifact.

The basic assumption for quantitative XRPD is that the material consists in a homogeneous population of randomly oriented crystallites. In reality, many archaeological polycrystalline products are inhomogeneous: they exhibit non-uniformities such as large variation in the grain size, large absorption contrasts, presence of many phases, differences in chemical composition, anisotropic orientation of the grains, presence of a substrate, and poor crystallinity. The specific features of synchrotron radiation (energy tunability, higher photon flux, and higher resolution) can help to solve part of these problems. These characteristics make SR-XRD a really powerful method for the study of CH.

Due to the huge number of applications of XRD to archaeometric and conservation problems, it is impossible to offer an exhaustive review and hence only some particularly representative case studies will be discussed here.

One of the most famous examples which illustrate the possible applications of non-destructive synchrotron-XRPD - complementing other standard analytical tools - in the study of CH, is the investigation performed by Doorhyee and co-workers [1-3] on ancient Egyptian cosmetics. In this project, synchrotron micro-beam techniques like μ-XRF, μ-XRD and μ-XANES were combined in order to identify selectively the phases and the trace elements present in different populations of grains representative of the powders, and to perform a quantitative determination of the different phases forming the cosmetics.

A large number of cosmetics, used in Ancient Egypt and held in the Louvre Museum, was analyzed. The study revealed a great variety of compositions using lead compounds and an advanced know-how in chemical synthesis. This shows that 4000 years ago, people already wanted more from their cosmetics than simply highlighting the eyes. The study also includes the analysis of the Bragg line profiles in relation to the microstructure of some minerals (size and distortions of the grains). In particular, among the compounds found in the studied mixtures, two natural phases were identified: black galena (PbS) and white cerrusite ($PbCO_3$) (Figure 1). Galena is a component

still used in North Africa as a base for many traditional cosmetics (like khols); white cerrusite enters the composition of white-to-grey powder make up. Both galena and cerrusite are rather common minerals which can be found in the region of the Red Sea. More surprisingly, the analyses revealed the presence of two other white components: laurionite (PbOHCl) e phosgenite ($Pb_2Cl_2CO_3$) (Figure 2). These phases are very rare in nature and could not have been extracted from the mines in sufficient quantities for the preparation of the cosmetics. In fact, one must consider that in the ancient Egypt cosmetics were extensively used by both women and men over a period of at least eight centuries. These compounds could in principle have been formed for alteration of the basic components by chlorine, but no foreign cations or chlorinated phases were detected in the more than 50 analyzed samples. Therefore the alteration of natural lead minerals within the make-up is unlikely. Hence, the conclusion was that laurionite and phosgenite were synthesized artificially. The synthetic origin of PbOHCl e $Pb_2Cl_2CO_3$ was confirmed by the analysis of the diffraction peak profiles, comparing the effects due to strains and to the crystallite dimensions with those present in the natural phases. It resulted that galena present in the cosmetics was crushed, probably to confer the desired texture and brightness the make-up. On the contrary, the peak profiles of laurionite and phosgenite were lacking of strain effects, suggesting that the crystallites were produced by direct synthesis.

Now the question is: why produce white components to be added to galena when cerrusite was available? The answer can be found in the historical hieroglyphics. In the ancient Egypt, cosmetics were not only used for aesthetic purposes but also for their therapeutic and magic properties The Greco-Roman texts mention that the white precipitates synthesized by PbO are good for eye and skin care. These lead compounds could be used as bactericides and as a protection for the eye against exposure to the sun's rays.
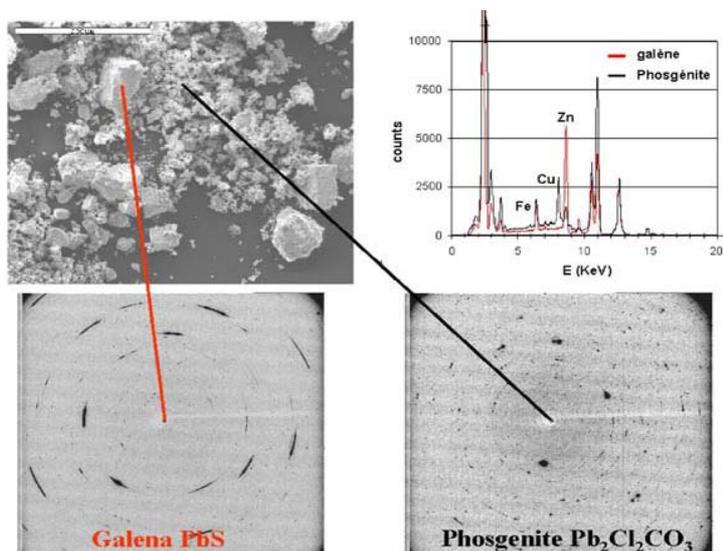

Figure 1 - (Top left) SEM picture of the archaeological sample (AF167) probed by the X-ray micro-beam (ESRF, ID22). (Bottom left) 2D transmission X-ray micro-diffraction pattern showingthe presence of galena powder in the AF167 sample (spot 1). (Bottom right) 2D transmission X-ray micro-diffraction pattern showingthe presence of phosgenite powder in the AF167 sample (spot 2). (Top right) XRF micro-fluorescence patterns recorded over samples AF167 and MG14400b, showing the impurity contents.
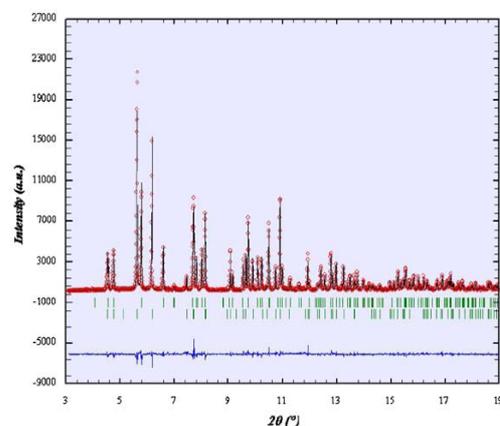
Figure 2. Observed (circles) and calculated (solid line) diffraction profiles of $2PbCO_3.Pb(OH)_2$ cerussite ($PbCO_3$), using the Rietveld refinement method. The markers indicate the position of the Bragg lines

A second very interesting example of application of synchrotron XRD to CH is the study of the pigment Maya Blue [4-6]. The composition of Maya Blue has confounded researchers for decades. How could the bright turquoise hue and extreme stability of this hybrid organic/inorganic pigment

be explained? How did the Maya combine skills in organic chemistry and mineralogy to create an important technology – the first permanent organic pigment – by binding indigo dye to a clay mineral substrate? Maya blue was first produced by the Mayas about the 8th century AD and extended well into the Spanish colonial era before the technology was lost. Due to its attractive turquoise color and light fastness, Maya blue was widely used in mural paintings, ceramics, codices. Maya blue is extremely stable: it can resist the attack of concentrated nitric acid, alkali and organic solvents without losing its color.

It has been demonstrated that Maya blue is a complex formed between palygorskite (or sepiolite) clay and indigo dye obtained from the common plant indigofera suffruticosa. However, a simple mixture of palygorskite and indigo is not resistant to chemical attack: the dye/clay mixture requires heating to 100 ∘C to produce Maya Blue. Although the pieces of the puzzle – indigo and palygorskite clay – had been identified, researchers have struggled since to explain how they fit together to create a material with such remarkable properties. However, now there is at least a plusible model for the locking of the indigo molecules on the surface of the paligorskite fibres. This model, proposed by Chiari et al. [4] on the basis of synchrotron and neutron XRPD, ESEM, thermogravimetric analysis and chemical modeling calculations, suggests that indigo does not enter the channels but is adsorbed in the grooves, which cover the faces of the fibres (Figure 3). The water adsorbed in the grooves can be removed at the temperature of formation of Maya blue (100 ∘C), thus leaving room for indigo. The amount of dye filling the grooves is in agreement with the thermogravimetric measurements and the occupancies derived by the synchrotron refinement.
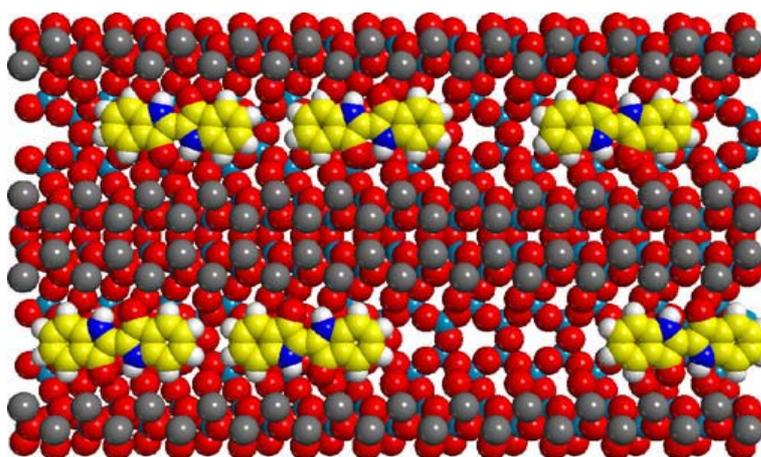

Figure 3 - Drawing of the groove with indigo molecules randomly distributed (*Yellow*), projected on the (010) face of palygorskite (H = *White*; C = *Yellow*; N = *Blue*; O = *Red*; Si = *LightBlue*; Mg = *Gray*) [4].

Archaeometrical applications of X-ray Absorption Spectroscopy

XAS techniques offer a combination of features particularly well-suited for the chemical analysis of rare, ancient materials and works of art. The methods are noninvasive, have low detection limits, afford high lateral resolution, and provide exceptional chemical sensitivity. They can be applied in air and virtually do not require any restriction on the type and size of the sample, which can be metal, ceramic, glass, cloth etc. and, finally, it is applicable to most of the elements of interest, even with very low concentration. 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 [7-8].
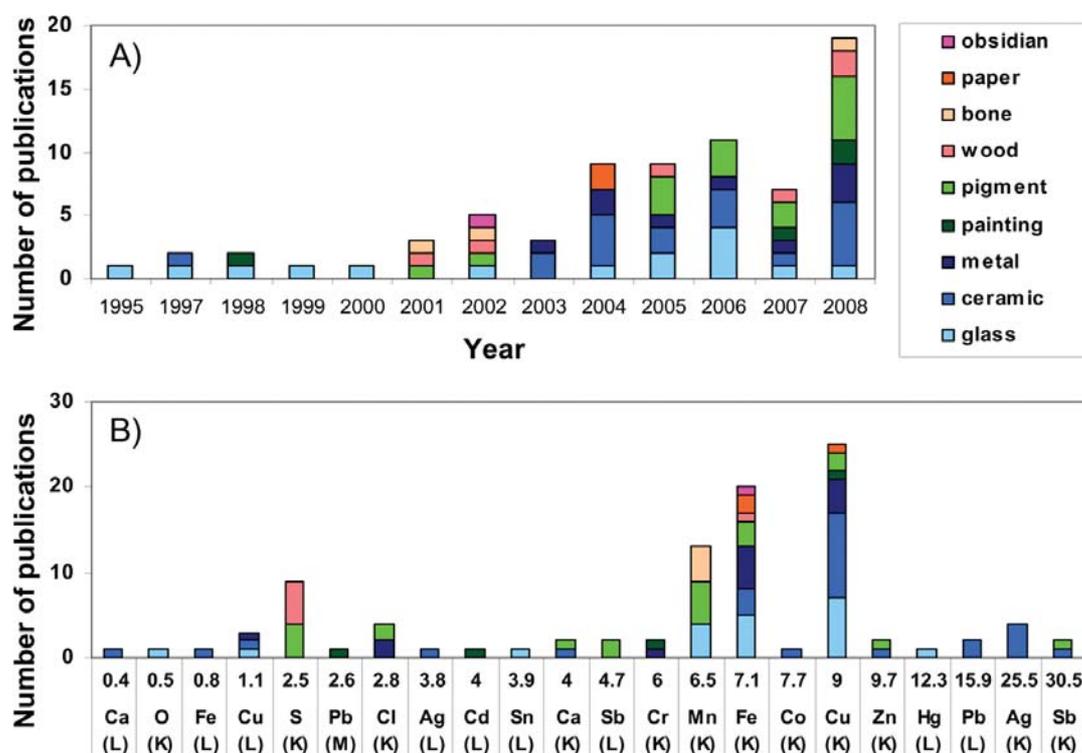
FIGURE 4 - Evolution of the publications reporting XAS analyses on CH items over the past decade. Statistics are sorted by type of material (A) versus time and (B) versus elements and absorption edges [7].

As shown in Figure 4A [7] 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. 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.

XAS techniques were first applied to the study of **ancient glass** [9, 10]. More recently, glazes and ceramics, based on similar vitreous matrices, have also benefited from an increasing interest. Indeed, XAS techniques are particularly adapted for the study of these types of materials. The good match between method capabilities (short-range probe, chemically sensitive) and material properties (amorphous and diluted state), makes XAS an unique tool in this field.

Variations of color 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. This explains the high number of XAS studies at the K-edge of these elements (Figure 4). For instance, XANES analyses at the Fe and Mn K-edges of ancient glasses from Sicilian archaeological sites in the Messina Province (Patti roman villa [11] and Ganzirri site [12]) and of medieval glass from Val Gargassa glasswork [13],

supported the hypothesis that pyrolusite (MnO2) could have been added intentionally as a decolorant during the melting procedure.

Many of the above-mentioned optical effects (such as color and transparency) can also 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 leads to opacification and a change in color (brown) of the glass panes.

XAS can also be exploited, together with SR-based X-ray fluorescence and XRPD, to study the **opacifiers** used to confer different colors to opaque glass, as was done in Roman glass mosaic tesserae [15, 16] or on Etruscan glass vessels and beads [17]. The first work was devoted to the characterization of a suite of very rare, highly decorated and colored glass vessels and beads from the VII to the IV century BC. The most serious difficulty in developing this study was that any sampling – even micro-sampling – was absolutely forbidden. As a consequence, the mineralogical and chemical nature of chromophores and opacifiers present in these Iron Age finds were identified by means of the following synchrotron-based, strictly nondestructive, techniques: micro X-ray fluorescence (μ-XRF), Fe K-edge micro X-ray absorption near edge spectroscopy (μ- XANES) and X-ray powder diffraction (XRPD). The μ-XRF mapping (Figure 5) evidenced high levels of Pb and Sb in the yellow decorations and the presence of only Sb in the white and light-blue ones. Purple and black glass show high amounts of Mn and Fe, respectively. The XRPD analyses confirmed the presence of lead and calcium antimonates in yellow, turquoise and white decorations. Fe K-edge μ-XANES spectra (Figure 6) were collected in different colored parts of the finds, thus enabling the mapping of the oxidation state of these elements across the samples. In most of the samples, iron is present in the reduced form Fe^{2+} in the bulk glass of the vessels, and in the oxidized form Fe^{3+} in the decorations, indicating that these glass artifacts were produced in at least two distinct processing steps under different furnace conditions.

XAS has also been applied to the study of **lusters** [17, 18], a decoration typical of the Medieval and Renaissance pottery of the Mediterranean basin, consists of a metal-glass nanocomposite thin layer embedded in a glass matrix (Figure 7). TEM measurements showed that luster consists of a thin film composed by a heterogeneous distribution of silver and copper nanoparticles of sizes ranging from 5 to 100 nm. These decorations show peculiar optical properties, producing brilliant reflections of different colors, cangiant effects and iridescences. The origin of luster decoration technique is one of most complex and fascinating issues of the ceramic history. Its preparation, described by Cipriano Piccolpasso in 1557, is one of the most complex to realize, and, surprisingly, the formation of the nano-particles is strongly analogous to that found in Roman red mosaic tesserae [15] and in the modern synthetic metal-glass nanocomposites.

Following the pioneering transmission electron microscopy studies, a number of projects dedicated to luster characterization by EXAFS and XANES were performed aiming mainly at establishing a correlation between color (red, gold, or green), chemical composition, and copper or silver oxidation states.

The main results of the spectroscopic investigations of luster are the following:

i)   In gold luster, elemental silver and copper are present at concentrations of about 20 and 1–3 wt. %, respectively, distributed within a thin layer from 60–120 nm depth. Metal nanoparticles are virtually made up of silver only, being copper mostly or exclusively present as Cu^+ and Cu^{2+} ions in the matrix.

ii)   In the case of red luster, elemental copper is present at about 8 wt. % distributed within a thicker layer, from 60 to 180 nm, with no silver. Nanoparticles of copper are present. However, only a minor fraction of copper is in the reduced metallic form (~20%), being mostly copper in the form of Cu+ surrounded by the nonbonding oxygen of the glaze matrix.

iii)   The gold and red colors can be attributed mainly to the silver and copper nanoparticles, respectively. The fact that in both gold and red luster, copper is significantly present in oxidized

forms explains the failure of previous attempts, carried out by XRF or inductively coupled plasma atomic emission spectroscopy, to put in relation the elemental copper/silver ratio with the luster color. The chromatic effects are determined only by the fraction of metal ions reduced to nanoparticles.

iv)   In red luster, characterized by a large quantity of Cu+, the higher polarizability and the smaller ionic radii of the exchanged Cu+ ions compared to that of the substituted alkali are responsible of a local structural rearrangement of the glaze matrix. The local modification could modify the refraction index of the glassy host, therefore influencing the luster optical properties.
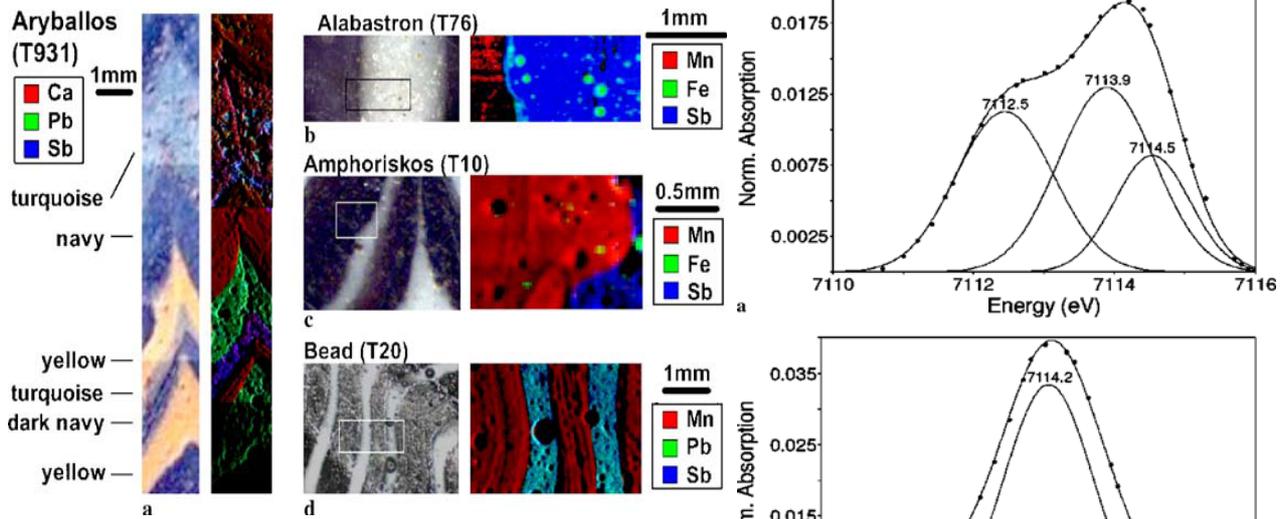
Figure 5 - Visible images and elemental mapping obtained by μ-XRF and represented with RGB visualization. (**a**) Aryballos T931; (**b**) Alabastron T76; (**c**) Amphoriskos T10; (**d**) bead T20. A logarithmic scale was used for the Alabastron sample. Legend scales are given for fluorescence maps [17].

Figure 6 - Normalized Fe K pre-edge spectra (*dots*) and the best fit calculated for: (**a**) bulk dark-navy glass, (**b**) yellow decoration, (**c**) turquoise decoration of Aryballos T931 [17].
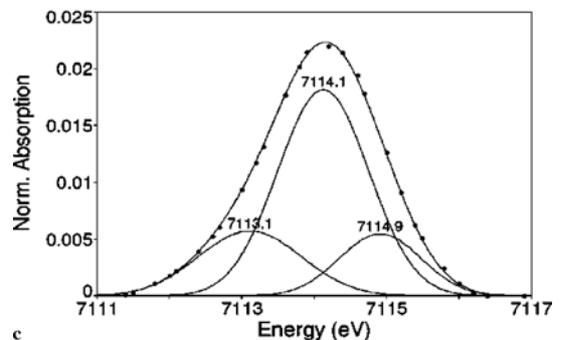
Figure 7 - Luster decorations on Italian Renaissance ceramics from Deruta (1530)

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 [20] or for the characterization of black pigments found in Spanish and French prehistoric caves [21-23] (Figure 8).

Several atypical manganese oxide minerals such as manganite, groutite, todorokite, and birnessite were identified in this last study. 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 non-local geological sites and may have had to be imported from a distant location.

Figure 8 – Paleolithic paintings from caves in Spain

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 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 [25] are subject to oxidation.

Another interesting application of XAS to the study of alteration phenomena concerns the blackening of copper resinate in a XV century Italian painting [26]. The study was aimed at providing structural information of the oxidation states and the local chemical of copper in the unaltered and blackened pigments, in order to elucidate the discoloration mechanism. EXAFS analysis evidenced that the local chemical environment of Cu in copper resinate can be described using neutral copper acetate as a model. It consists, essentially, of bimetal Cu^{2+} carboxylate complexes with a distorted octahedral coordination. Such a structure is retained, with some differences, in the blackened pigment. The alteration takes place without change of the valence state of Cu^{2+} ions, and the formation of the copper oxides CuO and Cu_2O responsible for the embrownment is excluded. Discoloration of copper resinate may be related to the local modification of the copper coordination structure, evidenced by the increase of the Cu-Cu and Cu-C distances in the EXAFS spectra.

Synchrotron-based Fourier transform infrared micro-spectroscopy applied to CH

Synchrotron-based Fourier transform infrared micro-spectroscopy (SR-FTIR) is one of the emerging techniques increasingly employed for CH analytical science [27]. Such a technique combines the assets of FTIR spectroscopy (namely, the identification of molecular groups in

various environments: organic/inorganic, crystallized/amorphous, solid/liquid/gas), with the extra potential of chemical imaging (localization of components) and the properties of the synchrotron source (namely, high brightness, offering high data quality even with reduced dwell time and reduced spot size).

This technique can be applied to nearly all kind of materials found in museum objects, going from hard materials, like metals, to soft materials, like paper, and passing through hybrid materials such as paintings and bones. The purpose is usually the identification of complex compositions in tiny, heterogeneous samples, and hence, a good example is the application of SR-FTIR to the analysis of ancient cosmetics [28], which are heterogeneous at micron scale and may be composed of a mixture of organic and inorganic phases. The study of such samples requires non-destructive techniques, with high detectivity, high lateral resolution, and high chemical sensitivity (atomic, molecular and structural probes). The studied sample originated from a 33 centuries old Egyptian cosmetic. New insights into the composition and spatial location of both organic and mineral components were obtained. Five different particles were analyzed and delivered similar findings: the core is fat rich, and surrounded with a mineral phase. In two particles, lead palmitate was clearly identified as a major component. Phosgenite ($Pb_2CO_3Cl_2$), a lead salt synthesized in aqueous solution, was also located in region near the surface of the particles.

SR-based Techniques for Nondestructive Subsurface Analysis of Painted CH Artifacts

High energy X-ray radiations are particularly suited for studies of **paintings** [29]. Studies can be performed directly on the entire painting such as, for example, by K-edge imaging (radiography with X-rays of energy below and above the absorption edge), which will offer a direct visualization of the elemental distributions at the painting scale. But, analyses are generally carried out on micro-samples taken from the art work.

The success of synchrotron techniques for such studies is linked to the intrinsic characteristics of the paintings that make classical analyses very hard. First, the amount of matter is usually tiny (less than 1mm thickness), hence requiring sensitive techniques. Second, paintings always exhibit multi-layered structures, with layer thicknesses of ~10 μm; this leads to the favoring of micro-imaging techniques, with a good lateral resolution (about one micrometer). Third, painting fragments are very complex in their chemistry, as they are made of mineral and organic matters, amorphous and crystallized phases, major and minor elements. Accordingly, a multi-modal approach is usually essential to solve the chemical complexity of such hybrid materials. In particular, the combination of micro X-ray fluorescence, micro X-ray absorption near edge spectroscopy (XANES), micro X-ray diffraction and micro-FTIR (infrared) spectroscopy is a key tool for the complete elucidation of painting compositions in order to derive information on its history (like painter techniques, pigment synthesis, authentication) and on its preservation for the future (mechanisms of degradation, processes of restoration).

As an example, the combination of micro-X-ray fluorescence (μ-XRF) and micro-X-ray spectroscopy (μ-XANES) was successfully employed for the visualization of a lost painting by Vincent van Gogh [30]. Vincent van Gogh (1853-1890), one of the founding fathers of modern painting, is best known for his vivid colors, his vibrant painting style, and his short but highly productive career. His productivity is even higher than generally realized, as many of his known paintings cover a previous composition. This is thought to be the case in one-third of his early period paintings. Van Gogh would often reuse the canvas of an abandoned painting and paint a new or modified composition on top. These hidden paintings offer a unique and intimate insight into the genesis of his works. Yet, current museum-based imaging tools are unable to properly visualize many of these hidden images. Synchrotron radiation based X-ray fluorescence mapping was applied to visualize a woman's head hidden under the work Patch of Grass. The scientists recorded

decimeter-scale, X-ray fluorescence intensity maps, reflecting the distribution of specific elements in the paint layers. In doing so they succeeded in visualizing the hidden face with unprecedented detail. In particular, the distribution of Hg and Sb in the red and light tones, respectively, enabled an approximate color reconstruction of the flesh tones. This reconstruction proved to be the missing link for the comparison of the hidden face with Van Gogh's known paintings (Figure 9).
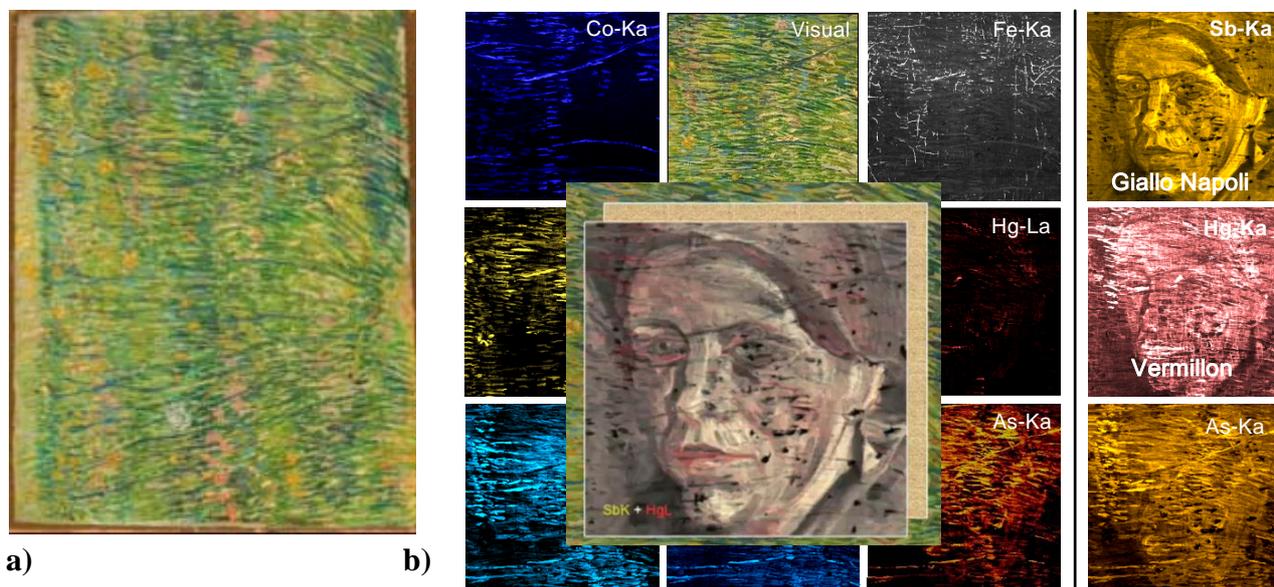

Figure 9 - a) Vincent van Gogh: Patch of Grass (Paris, 1887). b) Synchrotron radiation X-ray fluorescence maps, and reconstruction of the hidden image by combination of the Sb and Hg maps [30].

X-ray Computed Tomography applied to CH

Born in the early Seventies for medical applications, X-ray Computed Tomography is currently playing an increasingly important role in the field of Cultural Heritage diagnostics. In fact it represents a powerful non-destructive investigation technique, capable of displaying in a three-dimensional way the volume and the internal structure of the investigated objects, also thanks to modern 3D rendering techniques. This kind of information is very important for determining adequate conservation and restoration procedures [31, 32]. Advanced synchrotron sources have increased the interest in this technique [33-35].

An example of application is the study of an early 16th century prayer nut, one of the most fascinating objects in the Rijksmuseum (Amsterdam, The Netherlands) [36]. This spherical wooden object measures 4 cm in diameter and consists of two hemispheres connected with a small hinge so that it can be opened (Figure 10). The interior of the nut holds wood carvings with scenes from the life of Christ. These miniature relieves show an incredible degree of finish with carving details well beyond the millimeter scale. Synchrotron-based computer X-ray tomography revealed the structure and fabrication method of the bead. The central part of the relief was cut from a single piece of wood, rather than assembled from multiple components, underlining the extraordinary manual dexterity of its maker. In addition, a piece of fibrous material contained in the inner structure of the bead is revealed. This may have served as a carrier for an odorous compound, which would be in line with the religious function of the prayer nut.

Figure 10 - Left - Boxwood prayer nut with Christ carrying the cross and the crucifixion, c. 1515, Rijksmuseum, Amsterdam, The Netherlands. Right - Upper row: volume reconstructions with a vertical cut through the middle of the nut, revealing the shell structure as well as the knot sandwiched between the outer and inner shells. Note the openings in the outer shell. Lower row: volume reconstruction of the outer shell with Gothic motif.

Present ad future trends

The application of SR-based methods to Cultural Heritage Science has significantly consolidated since the first case studies, especially due to the evolution of instrumentation, radiation sources, experimental approaches [see for a review 37, 38].

The recent trends which are sensitive to evolution of the SR-based techniques can be summarized in the following:

1- there is a general and strong tendency towards the use of micro-beams, in particular devoted to μ-IR, μ-XRD, μ-XAS, μ-XRF, to produce 2D mapping. In these fields SR has maintained a leading position due to its intrinsic characteristics.

2- 3D imaging will undergo strong developments, both by using neutrons and synchrotron radiation.

3- Another general trend is to make use of multi-technique approaches, again based on micro-beams. Indeed, the possibility of simultaneously obtaining high quality data by several techniques on μg -quantities of material is considerably extending the information that we can obtain on micro-samples. The flexibility of the instrumental configurations at synchrotron and neutron sources is also a bonus parameter that makes large-scale facilities invaluable for almost any experiment that one may think of.

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