The surface of cultural heritage artefacts: physicochemical investigations for their knowledge and their conservation

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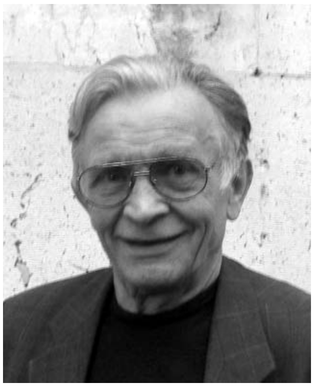
This *tutorial review* intends to show, through demonstrative examples chosen from the recent literature, how surface characterisation conducted by modern investigation methods leads to very rich information on a cultural heritage artefact's history, fabrication techniques and conservation state. Application of surface science to conservation science is of great help for the definition of a conservation and restoration policy for museum and archaeological objects. A brief description of the investigation methods is given, together with relevant references for more detailed information.

1 Introduction

The study of cultural heritage artefacts and the preparation of a preservation and restoration intervention begins with—and is often limited to—a comprehensive characterisation of their surface. This is not only true for museum objects, but also for archaeological artefacts, because the object as it was discovered may contain invaluable hidden information that could be lost by too much invasive intervention. The scientific investigation of a cultural artefact has thus to be negotiated with the "owner", the museum curator, archaeologist, conservator or restorer, and conducted as far as possible by non-destructive observations and analyses from its surface as it appears when it comes to the laboratory. Another constraint of cultural heritage objects is their accessibility: surface investigation of small size flat paintings may be conducted without problem in a modern laboratory, if the "owner" allows its transfer, but the problem is clearly different for very large artefacts, monuments or sculptures with a complex shape. The investigator may thus have to find or imagine a way and the equipment to perform *in situ* analyses or measurements.

The present article intends to show through demonstrative examples how complete and valuable physicochemical investigation of the surface of artefacts of cultural heritage brings important information. These data on their physical constitution, their authenticity, their history, the circumstances of their elaboration, their behaviour after being abandoned and/or stored, are useful not only to increase the knowledge of civilisation, history of techniques and art evolution, but also to elaborate a conservation policy.

It is necessary as a preliminary, to define what will be called "surface" in the present approach. The physical definition of a material surface is the first atomic or molecular layer in contact with the environment. The definition adopted here is more general: we consider the surface as a region with specific properties different from the bulk, extending from the physical surface to a more-or-less deep thickness. It could be a thin layer with a different composition (*e.g.* a varnish or a metal patina), a mechanically or physically perturbed region (*e.g.*



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tool roughening or intentional or unintentional coloration), a corrosion product layer, *etc.*

The application of surface science to cultural heritage materials has undergone dramatic development over the past decades, thanks to the impressive improvement of the analysis and investigation equipment. A short comparative overview of some characterisation methods will be given in the first part of this review, showing the importance of the combination of several methods. The following sections will try to illustrate our demonstration through concrete examples chosen from the recent scientific literature with respect to their diversity and their specific utilisation of particularly innovative approaches.

2 Surface investigation methods for cultural heritage objects, a summary

As mentioned, the specificity of cultural heritage object characterisation means that the methods used must be classified clearly in terms of their invasive character. Several recent publications[1] have been devoted to the description of most investigation methods applied in the field, and this section shall bring only a summarised overview of them, sending the reader to the cited publications to obtain more details on their performance. Tables 1–3 summarise the interesting performances of some methods in terms of application to cultural heritage objects. Among the enormous number of available characterisation methods, the list is restricted to the ones used in the following examples of the present article. For each method, further details are given in the following sections when it is introduced for the first time. The definitions of the numerous acronyms used in the tables and in the text are given in the appendix.

2.1 Non-destructive methods (Table 1)

Most methods mentioned in Table 1 have been impressively improved in their performances during the past decades. The most spectacular improvement is the miniaturisation of several types of equipment (XRF, μRaman spectrometry, AFM, spectrophotometry, XRD soon) which allows precise *in situ* analyses of the objects and paintings in their natural or exhibition environment. Another important development is the increasing access of cultural heritage research to heavy equipment such as particle accelerators (for PIXE, RBS, NRA and ERDA) or synchrotron radiation facilities (for μXRF, μXRD, XANES, EXAFS, *etc.*), which were, until recently, reserved to purely fundamental programs on laboratory materials. From the performance viewpoint, the improvements are to be found in the spectacular decrease in the size of the analysed volumes, thus improving the resolutions, both lateral and in-depth, from the surface.

Several methods do not strictly analyse the surface (*e.g.* XRD, XRF, analytical SEM, PIXE, FTIR) and, especially when it is impossible to complete the investigation by invasive methods, it is important to know exactly what the thickness analysed is and to try to use a complementary in-depth profiling method (for instance RBS to complete PIXE, see example below).

Table 1 Non-destructive characterisation methods applied to cultural heritage goods

Method[a]	Incident radiation or item	Detection	Information	Analysed depth	Depth resolution	Lateral resolution	First mention and description in section
Eye examination[b]	Light	Light	Shape, colour, topography	First layer	First layer	mm	3.1
Optical microscopy[b]	Light	Light	Shape, colour, topography	First layer	First layer	μm	3.1
SEM, ESEM, EM-EDS, EPMA	e^-	e^-, X-ray	Topography and elemental analysis	μm	μm	100 nm (structure), μm (analysis)	3.1, 3.2 (ESEM)
XRD, μXRD[c]	X-Ray	X-Ray	Compound crystallography	>10 μm	μm	mm to μm[c]	3.1
GXRD[c]	X-Ray	X-Ray	Compound crystallography	<100 nm	nm	cm	4.1
XRF,[b] μXRF[c]	X-Ray	X-Ray	Elemental analysis	>10 μm	>10 μm	mm to μm[c]	3.2
TXRF	X-Ray	X-Ray	Elemental analysis	<100 nm	<100 nm	cm	5.2
XANES, EXAFS[c]	X-Ray	X-Ray	Atomic environment	—	—	μm	6.1
Profilometry	Tip or light	Height	Surface topography	Roughness	μm to nm	mm to μm	3.3
AFM[b]	Micro tip	Height	Surface topography	First layer	<nm	<nm	3.2
FTIR	Infrared	Infrared	Compound and bonds	μm	μm	mm to μm	4.2
Raman, μRaman[b]	Light	Raman emission	Compound and bonds	μm	μm	mm to μm	3.3
PIXE	MeV ions	X-Ray	Elemental analysis	>10 μm	>10 μm	mm to μm	3.3
RBS, NRA, ERDA	MeV ions	Ions	Elemental in-depth analysis	>10 μm	10–100 nm	mm to μm	3.3, 4.2 (NRA)
Spectrophotometry[b]	Light	Light	Colorimetry	First layer	First layer	mm	4.1

[a] Acronyms are defined in appendix. [b] Portable equipment available. [c] Techniques available under synchrotron radiation.

Table 2 Micro-destructive characterisation methods applied to cultural heritage goods

Method[a]	Microsampling (size)	Incident radiation or item	Detection	Information	Analysed volume	Depth resolution	Lateral resolution	First mention and description in section
ICP-AES, ICP-MS	Chips (10 mg)	Plasma	Emission or mass spectra	Elemental analysis	mm^3	—	cm	3.3
SIMS, ToF-SIMS	Sputtering crater (100 μm)	keV ions	Secondary ions	Elemental analysis and bonds	First layers	1 nm to first layer	μm	4.2
LA-ICP-MS	Sputtering crater	Laser	Mass spectrometry	Elemental analysis	μm^3	<100 nm	<100 μm	6.1

[a] Acronyms are defined in appendix.

Table 3 Characterisation methods requiring large scale specimen destruction

Method[a]	Sample size	Incident radiation or item	Detection	Information	Analysed volume	Depth resolution	Lateral resolution	Description in section
TEM[b]	mm	e^-	e^-	Microstructure and elemental analysis	$\gg$μm^3	nm (on transverse section)	nm	4.1
SEM, SEM-EDS (transverse section)	<1 mm	e^-	e^-	Microstructure and elemental analysis	μm^3	100 nm	100 nm (structure), μm (analysis)	3.1
XPS	cm	X-Ray	Secondary e^-	Elemental analysis and bonds	<μm^3	<10 nm	mm to μm	5.3

[a] Acronyms are defined in appendix. [b] Recent developments (FIB foil preparation) may allow micro-destructive sampling.

Finally, even when the investigations are absolutely limited to non-destructive methods, it is strongly recommended to use several characterisation methods to compare the results and draw as accurate a scheme as possible of the hidden reality.

2.2 Micro-destructive methods (Table 2)

In this category are classified the methods for which the intervention on the object is of very small amplitude, barely visible by the naked eye, or easy to hide. The recent improvements of chemical analysis methods have made possible very accurate analyses on very small matter volumes sampled from the object, for instance by micro-drilling or scratching (ICP-AES, ICP-MS). On the other hand, ion or laser ablation methods (SIMS, LA-MS) can bring rather accurate analysis results issued from a local sputtering of the matter on a very small area. They shall surely undergo important development in the future.

2.3 Destructive methods (Table 3)

The methods usually classified as "surface analysis" methods (AES, XPS, *etc.*) do not strictly analyse the extreme surface. Even if the analysed area remains limited, the fact that the specimen has to be put under vacuum does not allow direct investigation of the objects. TEM is also very invasive because a quite large amount of matter has to be sampled to prepare the thin foil (about 0.1 μm) transparent to the microscope electrons. One must mention that the very recent perfection of the FIB equipment may be a very interesting track for the preparation of thin foils directly from a limited area of small objects.

2.4 Choice of method

In summary, the choice of a characterisation method for the specific study of cultural heritage artefacts is bound to the "agreement" with the object "owner" mentioned in the introduction. That choice will depend on the availability of the object to be transferred to the laboratory, on the nature and scale of the problem (*e.g.* simple observation of the state of conservation, large scale conservation work, knowledge of the surface for the preparation of restoration, deep investigation of the surface layers for a full conservation program, *etc.*), on the possible allowed microsampling or large sample subtraction, *etc.*

It is necessary to underline that, as for any material characterisation study, the comparison of the performances and application fields of the different methods imposes a necessary recourse to several complementary methods.

The investigation of cultural heritage objects may be greatly enriched by laboratory experiments on disposable specimens such as, for instance, artificially reproduced pigments or surface treatments using ancient retrieved recipes. That important method of understanding the origin and the mechanisms of the features observed on ancient artefacts is often a key procedure to be applied in order to propose a valuable conservation or restoration policy. It allows obviously the use of all characterisation methods available in a material science laboratory.

3 Metal-based objects

3.1 Looking for the original surface limit of archaeological metal objects

Recovering the shape and the surface details of an ancient metal object buried for thousands years in the soil is of utmost importance from an archaeological viewpoint. It requires the ability to locate its former surface among the corrosion products. Whether this former surface, termed the "original surface", is still kept in place or has moved from its original position among the corrosion products, one aim of the conservation treatment is to locate it and to eliminate deposits and corrosion products above it in order to reveal artefact's shape and decoration.

The long term corrosion mechanisms of metal objects are not completely identified nor quantified (see following section) but the macroscopic or microscopic features of corrosion products for the most current antique metal alloys are sufficiently well described to allow their qualitative identification by the conservators using observations under a binocular microscope or SEM and XRD investigations. SEM is used to image, at the microscopic scale, the surface of a specimen bombarded by a focused and scanned electron beam (probe diameter <1 μm). Emitted secondary electrons or backscattered electrons are detected and their signal is displayed on a cathodic screen in synchronism with the incident beam scanning, thus providing a virtual image of the surface. The secondary electron image represents the surface topography, whereas the contrast of the backscattered electron image depends on the surface composition. The incident beam also induces an X-ray emission, and the exploitation of the energy spectrum of that emission, recorded in a energy dispersive spectrometer (SEM-EDS) is used for quantitative elemental microanalysis; it is fully quantitative for elements heavier than carbon ($Z > 6$). When the object is small enough to be introduced in the specimen chamber of an SEM, it is possible to observe and to analyse the surface features or the corrosion products at the microscopic scale.

XRD brings a structural identification of the surface crystallised compounds, thanks to the determination of their crystalline systems and the measurement of their crystalline network parameters.

Systematic research has been conducted[2] in order to identify the markers in the microstructure of the corrosion products that indicate if the observed area belonged to the original metal or if it is a part of the corrosion developed outward from that original metal. The limit between both areas defines then the limit of the original surface. For instance, on heavily-corroded bronze objects, the region where a "ghost" structure of the metal microstructure is observed (*e.g.* traces of the former dendritic structure, Fig. 1) is clearly under the original surface, whereas a region containing silica crystals originated from the burying medium is to be attributed to external corrosion. The limit between them locates the original surface.

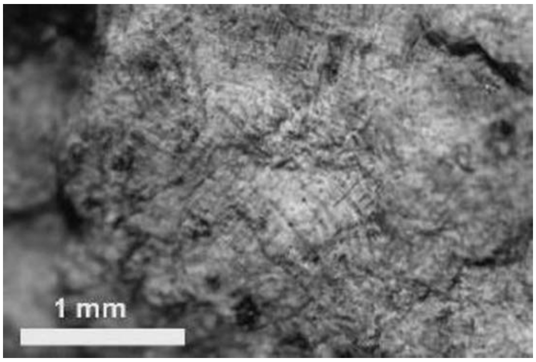

Fig. 1 "Ghost" dendritic structure remaining in the upper corrosion layer (bronze statue of Artemis found in Petra), under a binocular microscope.[2]

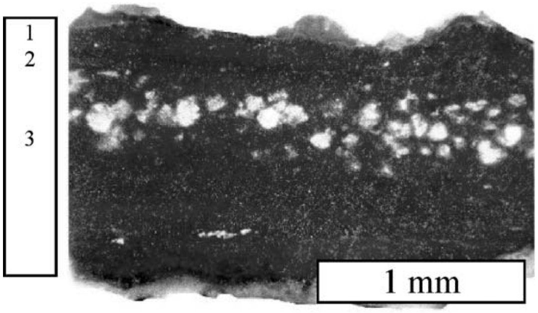

Fig. 2 Optical microscope full section of the copper Qumràn scroll.[2]

The quoted work draws a general picture for a logical classification of the corrosion products of any metal archaeological object and proposes a systematic procedure for the tracking of their original surface and the conservation action on the artefacts.

The case of the copper scroll of Qumràn discovered in a cave near the Dead Sea and dating from the beginning of the Christian era is a good example.[2] The surface of the scroll appears more or less uniform. The corrosion of this 1 mm-thick copper sheet has come to an end; there is no metal left. In Fig. 2 is shown the overall (from one face to the other) stratification of the corrosion products at the optical microscope scale. Moving inwards from both surfaces of the scroll, the following was observed:

- Layer No.1: an outer green layer, a few microns thick, mainly containing Cl, Cu and O. X-Ray diffraction reveals a preponderance of copper hydroxychlorides and basic carbonate (copper(II), mainly clinoatacamite and malachite). Inclusions are aluminium silicates, silica and Mg- and Ca-rich compounds.
- Layer No.2: a porous red copper oxide layer (copper(I), cuprite Cu_2O) between 30 and 100 μm thick, with the same inclusions as layer No.1.
- Layer No.3: a red copper oxide layer (cuprite) penetrating down into the heart of the sheet metal fragments. It comprises a series of sub-layers of varying thickness. Its main character is to contain small amounts of tin and numerous porosities.

The conclusion is that the original surface is situated at the interface between layer 2 and layer 3. The work of the conservator and restorer can then begin to loosen that surface and identify the inscriptions written on it. That work is facilitated by the fact that the interface is weak and easy to separate. This observation of the occurrence of the original surface between two cuprite layers, one outside containing silicon, and the other inside containing the alloying element Sn, is very often observed on archaeological bronze (Cu–Sn-based alloy) artefacts.

3.2 Metal corrosion, the natural patinas

The question of metal artefact corrosion has been the subject of a considerable amount of research, not only, as in the preceding section, for the qualitative identification and conservation of the original surface, but also for a comprehensive

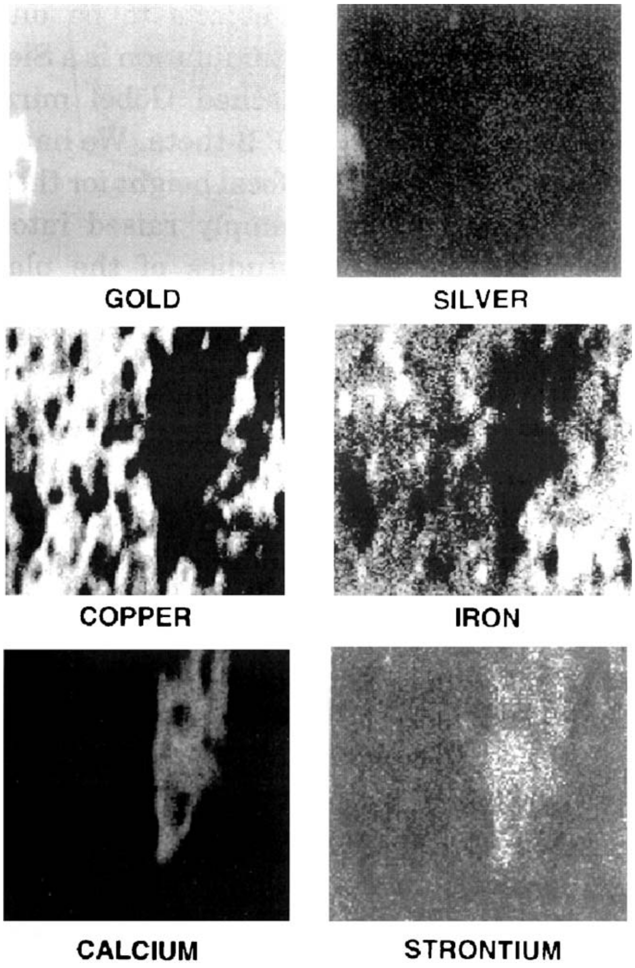

Fig. 3 Scanning elemental maps obtained by *in situ* μXRF on a Greek inscribed copper plaque (8th–7th century BC). Overall area is 2.3 × 2.4 mm^2.[3]

knowledge of the corrosion mechanisms and of the consequences for conservation science. When they are well preserved and continuous, the corrosion product layers are often called natural patina. Several examples[3] show the application of multiple investigation methods for a full description of the patina layers. The most usual methods for corrosion product non-destructive identification are XRF and XRD. The first produces an elemental analysis through an X-ray fluorescence emission spectrum under X-ray irradiation; it is fully quantitative for elements heavier than sodium ($Z > 11$); the second is shortly described in section 3.1.

An example is the analysis of the corrosion patina of a Greek inscribed plaque. By using portable micro-fluorescence (μXRF) equipment, it could be shown that small flakes of gold had been embedded into the corrosion layer, probably during burial (Fig. 3). XRF shows the presence of gold, silver and calcium in the analysed patina, while XRD at variable incidence angle allows the identification of cuprite (Cu_2O), malachite ($Cu_2CO_3(OH)_2$) and atacamite ($Cu_2(OH)_3Cl$) at different depth. The presence of atacamite is known to raise an alert toward the conservator because it could be a precursor of active corrosion.

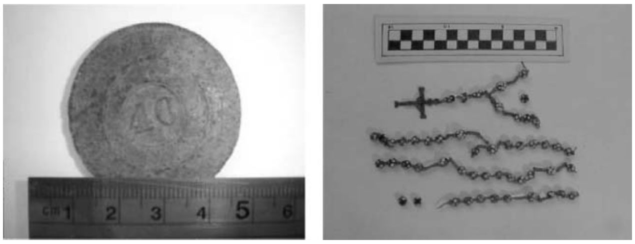

Fig. 4 Coin and rosary found in the Rochedo site (Brazil, state of Rio de Janeiro).[4]

In that case ESEM, for which a partial pressure of air or neutral gas is maintained during the observation in the microscope, may be of particular interest, because the presence of the gas eliminates the charging effect that appears on insulating specimens under an electron beam; it also preserves the integrity of the surface better than the usual full vacuum of current microscopes.

The work of Angelini *et al.*[4] on bronze artefacts (a coin and a rosary, Fig. 4) excavated from an ancient Brazilian sugar mill (17th century) in the region of Rio de Janeiro, is a good example of a comprehensive study combining the full identification of the metal and the corrosion products by analytical SEM-EDS and XRD, followed by a conservation treatment by PECVD (plasma enhanced chemical vapour deposition) of a SiO_2 layer to preserve the surface from further degradation.

The efficiency and structure of the SiO_2 deposit has been tested using electrochemical impedance measurements. Impedance data, measured on test specimens in a sodium chloride solution at the open circuit potential, have been analysed using a suitable fitting procedure in order to obtain the values of the charge transfer resistance (R_{ct}) and of the double layer capacitance (C_{dl}) which may be directly related to the protective properties of the coating: the higher the R_{ct}, the higher the barrier effect of the layer.

The surface quality of the protection treatment was controlled by the use of AFM. AFM enables the study of the electrically conductive or insulating specimen without specific preparation; the AFM consists of a microscale cantilever with a sharp tip (probe) at its end which is used to scan the specimen surface. Thanks to very sensitive displacement controls of the specimen and of the tip by piezoelectric tubes, the equipment allows a measurement of the surface topography with a precision of less than one nanometre in height and a few nanometres in lateral position.

In fact, one of the major concerns of conservators is the preservation of artefacts out of the excavation site, where they had reached equilibrium with the soil, but from which they were then disturbed by their discovery by the archaeologists and by the subsequent transfer to a deposit or museum. The artefacts need coatings that are reversible and with a good aesthetic appearance, which can act as an effective barrier against atmospheric pollution. The above-mentioned characteristics of PECVD coatings render those ideal candidates for this employment; furthermore, plasma processes can be preceded in the same chamber by proper cleaning or passivating surface treatments, which do not affect the bulk

Fig. 5 Example of black patinated antique objects (Louvre museum). Left: Roman ink pot of Vaison-La-Romaine Louvre DAGER; the himation inlay of Venus is patinated. Right: Egyptian feminine statuette Louvre DAE, the body is patinated.[6]

properties of the artefacts (see section 6.2 for another application of that kind of preventive treatment).

3.3 Intentional patinas on bronze artefacts

Another type of oxide layer reported on metal archaeological artefacts is the result of intentional surface treatments done by the ancient craftsmen in order to change the surface aspect and colour. During the past decade particular attention has been given to the so-called "black bronze" or "black copper" discovered on Egyptian (2nd millenary BC), Roman empire (1st century AD), Chinese (4th century AD) or Japanese (14th century AD) bronze objects.[5] It consists of a chemical treatment applied to specific copper alloys containing always gold (1–8 wt%) and eventually silver (1–4 wt%) in order to give them a black or velvet colour. A comprehensive study[6] has been conducted recently on a large corpus of Egyptian and Roman empire pieces from the French Louvre museum (Fig. 5). That study combines several non-destructive investigation methods of characterisation: optical microscopy, XRD, micro-Raman spectrometry and IBA analyses. Micro-Raman spectrometry (μRaman) is based on the measurement of the spectrum of the light emitted by an object illuminated by a monochromatic laser source (see section 5.1). The difference between the wavelength of light elastically diffused (Rayleigh emission) and that of the inelastic emission due to the interaction with atomic or molecular vibrations, gives information on the chemical bonds of the analysed compounds. When the incident beam is focused to the specimen surface through an optical microscope, the analysed area can be reduced to the order of micrometres and the in-depth analysis can be performed using confocal microscopy (if the material is sufficiently transparent).

The IBA methods used are PIXE and RBS.[7]

- PIXE is based on the X-ray emission induced by the surface bombardment of energetic particles. In the present case, the particle beam is either a 3 MeV proton or a $^4He^{2+}$ 6 MeV beam delivered in an open atmosphere by a pelletron accelerator. As for XRF, PIXE allows a quantitative elemental analysis of the surface layers, but with a better limit of detection. Thanks to the choice of the particle beam, it was possible to obtain the elemental analysis of the patina without interference with the underlying bulk alloy.

- RBS records the energy spectra of particles backscattered from the object, here 3 MeV protons or 3–6 MeV $^4He^{2+}$ incident particles, also in an open atmosphere. From these spectra, it is possible to infer the depth distribution of the elements over the first few micrometres (3–20 μm) from the surface, with a depth resolution better than 100 nm. The choice of the beam particles and energy is adapted to the desired thickness of investigation.

As IBA analyses need the knowledge of the substrate bulk composition, it is necessary to use a micro-destructive method to obtain that composition. Metal chips are sampled by micro-drilling (1 mm diameter hole) and analysed by ICP-AES,[8] a method which consists of digesting the sample in *aqua regia* and converting the solution to a plasma whose atomic emission is recorded to obtain the elemental composition.

Most of the black patinas appear to be pure cuprite Cu_2O, containing small amounts of gold and eventually silver. The natural colour of cuprite is red, and the role of the precious metals in its black coloration is still not well understood.

Table 4 shows a summary of some results of that investigation, concerning the nature and thickness of the black patina layers, obtained by the combination of several non-destructive methods.

One may mention that, in the course of that study, a new type of intentional patina was evidenced and analysed on the handle of a Roman empire strigil dated from the 4th century AD. In that case, the bulk alloy is brass (Cu–Zn alloy) and it was intentionally coloured in orange-red, probably also by

Table 4 Summary of the X-ray diffraction, μRaman and RBS in-depth analyses on antique intentional black patinas[6]

Object	Nature of the surface layer	Thickness/at cm^{-2}	Estimated thickness/μm
Harpocrate body (Egypt, XVIIIth dynasty)	Nantokite, clinoatacamite, trace of Au	38×10^{18}	5
Harpocrate lock of hair	Cuprite, clinoatacamite (traces), Au, Ag	$>10^{20}$	>20
Sobek counterpoise (Egypt, New Kingdom)	Cuprite, Au, Ag	$>10^{20}$	>20
Statuette robe (Egypt, 3rd intermediary period)	Cuprite, chlorides (mostly clinoatacamite), sulfides	70×10^{18}	9
Double aegis counterpoise (Egypt, 3rd intermediary period)	Cuprite, Au, Ag	$>10^{20}$	>20
Ink pot: Venus and Adonis' himation and Eros' wing (Rome, 1st century)	Cuprite, Au, Ag, malachite (corrosion)	$>10^{20}$	>20
Bistoury handle inlay (Rome, 2nd century)	Cuprite, Ag, malachite (corrosion)	$>10^{20}$	>20

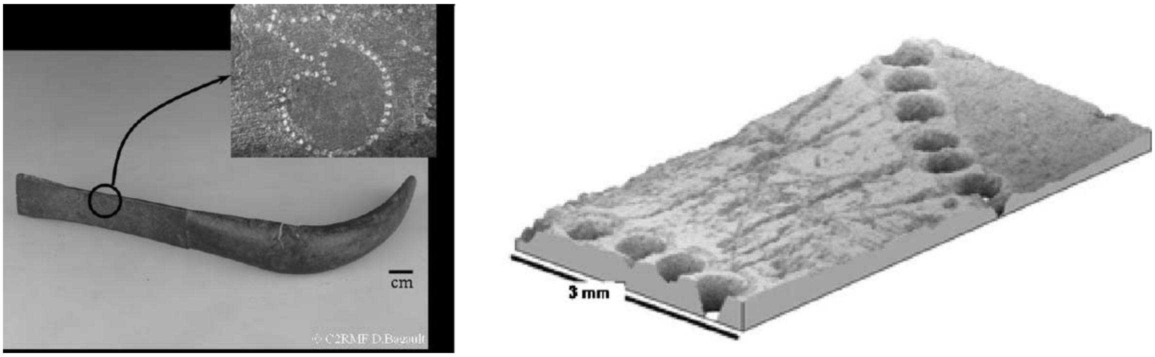

Fig. 6 Roman strigil (4th century) and profilometry images showing the microtopography around the patinated detail.[6]

chemical treatment (Fig. 6). An optical profilometry study, which evidences the traces left by the craftsman rubbing tool, showed that the patina was probably applied on the whole surface of the handle and then rubbed away from the region where it was not desired. The profilometry equipment used was a Stil optical bench: an objective with a strong chromatic aberration is focused on the surface and the reflected light is analysed by a spectrometer; the wavelength of the reflected light depends on the distance between the surface and the objective.

The attention given to bronze intentional patinas is quite recent, and this kind of investigation is very important to draw the attention of the museum curators and restorers to their existence, in order to avoid their destruction when the objects are cleaned or restored.

3.4 Organic-induced degradation

The problem of museum object alteration due to organic pollutants may become an important issue for the conservative prevention of cultural heritage artefacts. An example is the program conducted in France recently to preserve the lead seals used for the Papal bulls sent to the Catholic communities for centuries. Those seals were kept frequently in museum libraries inside oak furniture. But, during a very long period, oak wood emits several organic volatile compounds (OVC) such as tannic acid, acetic acid or formic acid, able to corrode heavily the lead objects kept in neighbouring areas (Fig. 7). The program of preservation included a full characterisation of the corrosion kinetics of lead in the aggressive atmosphere containing OVC, conducted mainly by IBA analyses (described in section 3.3), in an open atmosphere (Fig. 7), to measure the corrosion layer thickness non-destructively, and XRD (described in section 3.1) to identify the corrosion products, which are mainly lead acetates and carbonates.[9] Restoration procedures, based on electrochemical reduction of the corrosion products could be proposed and developed.

4 Ceramic and glass-based objects

4.1 Metallic lustre decoration on glazed ceramics

Among the very rich and various palettes of decorative effects developed by the potters on ceramic objects, one is particularly fascinating. Called ''lustre'', this technique seems to have been born in the 9th century, in factories created by the Arabs during their conquests in the Orient (Mesopotamia, Egypt and Persia). With the passing of the centuries, Arab potters spread their know-how all over the Islamic world. It reached Spain and was finally transmitted at the end of the 15th century to the Italian

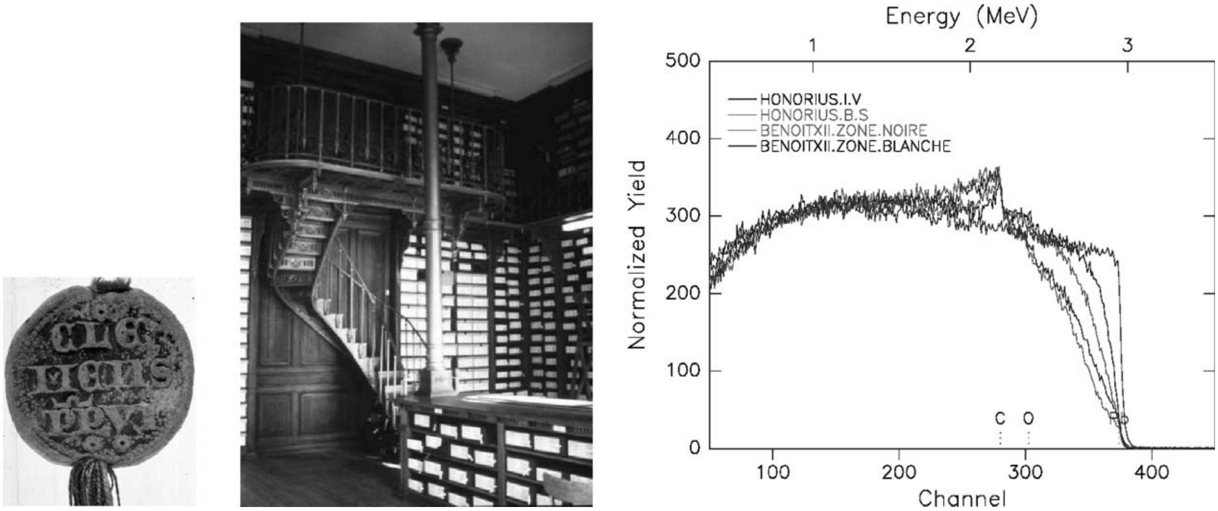

Fig. 7 From left to right: a Papal bull lead seal; oak furniture for seal storage (Bibliothèque nationale de France); RBS spectra showing the surface oxidation of seals.[9]

Fig. 8 Lustred ceramic fragments collected in Fostàt (two first lines) and imitation by a Spanish craftsman (third line). The white line represents 1 cm.[12]

Renaissance workshops, giving rise to the so-called majolica ceramics. Lustre was achieved by the application, onto the already glazed ceramic surface, of copper and silver compounds (oxides, nitrates, carbonates, sulfates…) mixed with clay or ochre and a binding agent. The ceramic was then fired again at 500–600 °C in a reducing atmosphere (smoke combustibles). This oxygen-free atmosphere induced the reduction of metallic compounds, resulting in the formation of an iridescent metallic film. A complete description of the reduced lustre technique and history may be found in the literature.[10]

Apart from the very interesting aspect of the transmission of such a sophisticated elaboration technique among the whole Islamic world throughout 7 or 8 centuries, lustred ceramics called the attention of conservators and scientists on account of the very particular structure of the surface film which is responsible of their specific aspect. Several investigations[11] have shown that the final firing treatments develop a very thin film on the surface, less than 1 μm thick, constituted of vitreous matter embedded in which are nanoparticles of metallic silver and/or copper. The resulting aspect is an iridescent shine which imitates sometimes a gold, a silver or a copper deposit in specular reflection and appears with various colours from deep red to bright yellow by diffused light observation.

A systematic study of lustred ceramic fragments has been conducted recently[12] with the use of several investigation methods: optical microscopy, SEM-EDS high resolution SEM, GXRD, AFM, PIXE and RBS. The specimens were a series of ceramic fragments collected in Fostàt (Egypt, in the region of Cairo) and dating from the 9th–10th century, which were compared to the recent work of a Spanish potter from Granada (Fig. 8).

Optical microscopy and conventional SEM-EDS (see section 3.1) showed that the coloured decoration consists of small particles of copper and/or silver (micrometric scale) in a glassy matrix. Thanks to high resolution SEM and AFM (high resolution SEM uses a field emission gun electron source and may be operated at very low accelerating voltage; AFM principle is described in section 3.2) it was possible to detail the fine microstructure of the surface layer (Fig. 9). The particles are in fact of nanometre size (10 nm for the smallest) and are clearly embedded, and often covered, by a glassy layer. They may be agglomerated in clusters of micrometric size.

GXRD (XRD is described in section 3.1, GXRD is XRD performed at a low X beam incidence angle) was performed to identify the nature of the particle, metallic copper and/or silver. Furthermore, the measurement of the metal diffraction line widening was used to calculate the smallest particle diameter, estimated to be 12 nm.

TEM has been performed on a sample taken from a modern disposable fragment (Fig. 10). TEM uses transmitted electrons (of 100 or 200 keV energy) to image the structure and obtain electron diffraction diagrams of a thin foil ($\sim$100 nm thick) of material. The observation confirms the presence of metal nanoparticles embedded in a glassy matrix. The surface is covered by a thin layer of vitreous glaze containing nearly no particles.

The use of IBA (PIXE and RBS, see section 3.3) brings a complete quantitative description of the stratigraphy of the different layers from the surface inward. It becomes possible, then, to measure the amount of copper and/or silver in the lustre, the thickness of the metal-free covering film and of the metal-containing layer and the extent of the gradient of metal particles from the latter layer into the glaze substrate. The knowledge of these parameters brings a very powerful and rigorous scientific set of criteria to characterise the evolution of the lustre elaboration technique through the ages and amongst the various and numerous dynasties of the Islamic world. This completely new approach is now under completion.[14]

Another approach to understand and prepare the conservation of these materials is to obtain a photometric description of

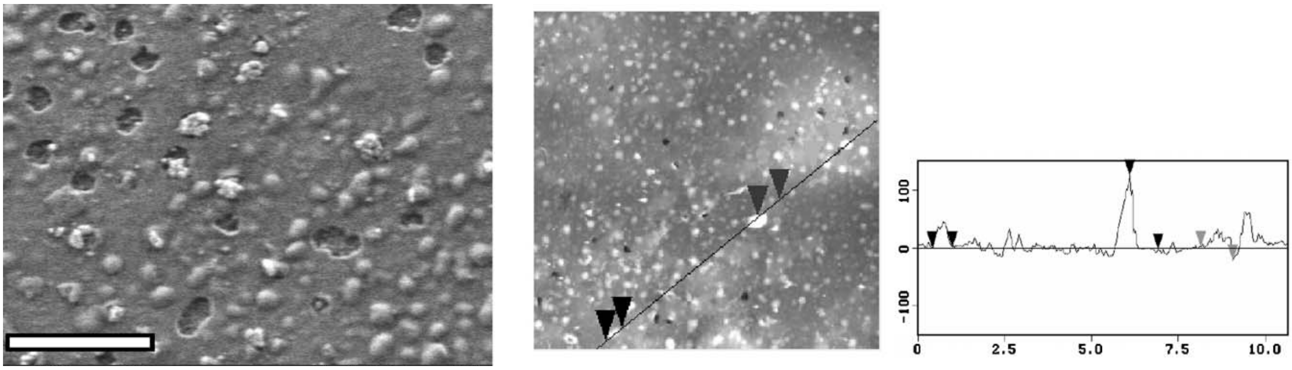

Fig. 9 High resolution SEM micrograph (left; the white line is 1 μm), and AFM topographic image (centre and right) (right; abscissa in μm, ordinate in nm) of a lustred ceramic surface.[12]

their aspect and colour.[12] This is possible using spectrophotometry in which the specimen is illuminated by a white light in the visible range, backscattered light is collected and the obtained diffuse reflectance spectra are, after normalisation to a white reference, recorded in the visible, 380–780 nm wavelength, range. The illumination-collection angle is chosen to be 22°, after a preliminary study showing that specular reflection is negligible at that angle, in the backscattering configuration. The obtained spectra are thus representative of the diffuse light aspect of the lustre. A suitable transformation of the spectral information gives the colorimetric coordinates of the analysed surface. The system used here is the so-called "CIE *La***b**" system, where *L* is the luminance and *a** and *b** are the colour coordinates. It is interesting to note that studies have shown that the coloured aspect of the lustre is not entirely correlated to the metal content of the surface film (Fig. 11, Table 5), unlike the common idea that copper produces the red colour and silver the golden-like one. In fact, the size and distribution of the nanoparticles in the film are also important parameters. Most of the lustres exhibit colour parameters not far from the gold colour parameters.

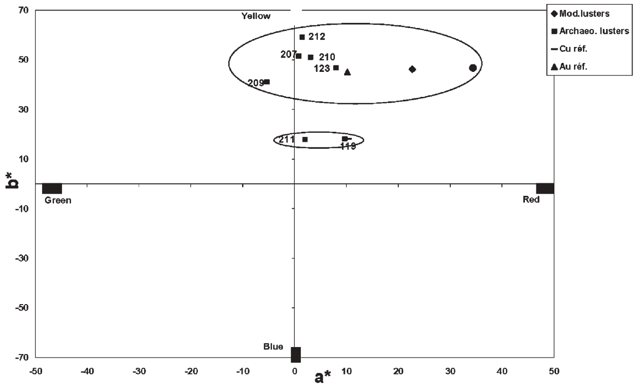

Fig. 11 Colorimetric coordinates (in CIE *La***b**) of the archaeometric and modern lustres.[12]

4.2. Glass weathering and degradation

It is well known that the surface of glass is very sensitive to environmental degradation and this is an important issue for the conservation of glass artefacts such as church stained glass windows and all kinds of glass art objects. A large number of studies have been devoted to the characterisation of glass weathering and the research of protection against the degradation. Studies such as these also bring important information on the authenticity of the artefacts. Examples are reported by Schreiner.[15] The methods used for these kind of studies are usually mapping SEM-EDS, XRD (see section 3.2) and μRaman spectrometry (see section 3.3). The composition of the glass used for stained glass fabrication has suffered important changes through the ages, and the medieval period, where the silica content was very low and where soda has been replaced by potassium hydroxide, is particularly unfavourable from the point of view of glass

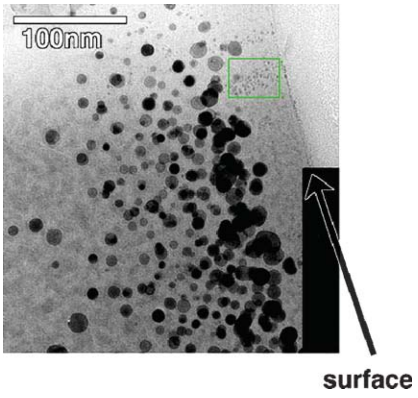

Fig. 10 TEM micrograph: transverse section of a modern lustred fragment.[13]

Table 5 Metal particle content of the archaeometric and modern lustres[12]

	Ag/10^{15} at cm^{-2}	Cu/10^{15} at cm^{-2}	Ag/Cu atomic ratio
Ancient lustres			
207	32.1	53.5	0.60
208	59	44	1.34
209	42.5	35	1.21
210	58	21	2.76
211	129	62.5	2.06
212	32.8	40.5	0.80
119	48.1	146	0.33
123	105.8	74	1.43
Modern lustres			
No. 1	134.5	91.5	1.47
No. 2	158	116	1.36

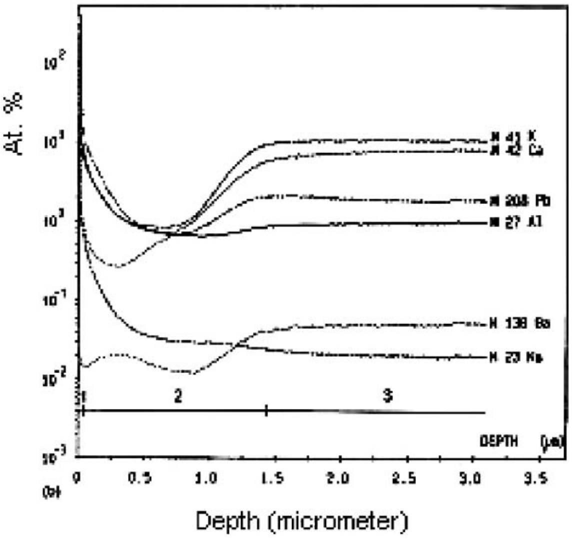

Fig. 12 SIMS quantified depth profile of elements in a medieval glass. Layer 1: outermost glass surface; layer 2: leached layer; layer 3 bulk glass.[15]

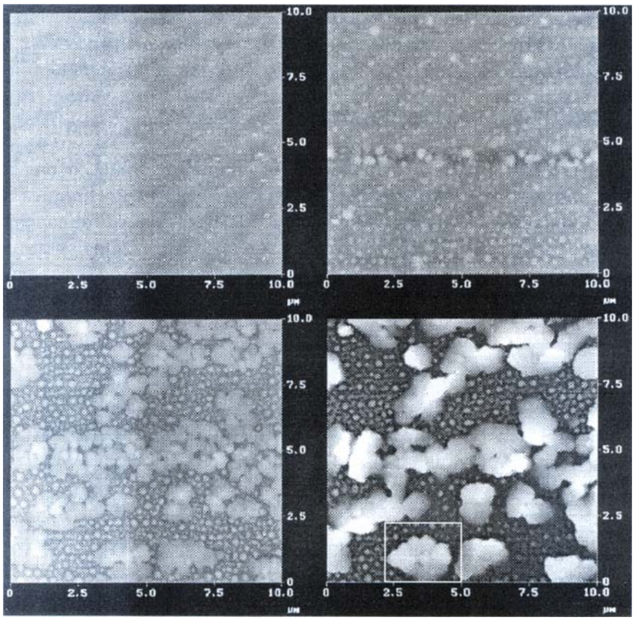

Fig. 13 AFM images of a cleaved glass surface exposed to nitrogen with 1 vol. ppm SO_2 and 70% relative humidity. The height range is 200 nm from black to white. Exposure times from left to right and top to bottom: 1 min; 4 min; 1 h; 6 h.[15]

durability. Three types of deterioration are observed and identified by SEM-EDS observation and analyses, depending on the chemical composition of the bulk: formation of a thick and hard crust containing calcium and potassium sulfates; pitting corrosion associated with local cracks; and simple iridescence on an apparently unaltered surface.

In order to identify the ion transport mechanism responsible for the first stages of the degradation, several investigations have used SIMS analysis. In this method, the secondary ions sputtered under middle energy (5 to 15 keV) ion bombardment are quantitatively analysed by mass spectrometry.[16] Thanks to the ion sputtering process, this method allows in-depth profiling from the surface of all elements, including hydrogen. The quantification of SIMS depth profiles is difficult, but it has the advantage of a very high sensitivity; it is furthermore one of the only methods (with NRA) that permits hydrogen analysis in materials. Fig. 12 shows an example of profiles obtained on a medieval glass. Very large amounts of hydrogen (up to 40 at%, analysed by NRA using the $^{1}H(^{15}N,\alpha\gamma)^{12}C$ reaction) are present in the so-called ''leached'' surface layer of the weathered glass. In fact, the corrosion involves an ion exchange process with sodium, potassium and calcium ions moving to the surface, being replaced by hydrogen ions from atmospheric moisture.

This phenomenon of ion exchange during glass weathering has been extensively studied on model specimens with various compositions and in various weathering media, by the combination of several investigation methods, such as SIMS, NRA, FTIR, μRaman spectrometry and AFM. NRA is an IBA analysis method which uses the energy spectrum of the nuclear reaction products resulting from the interaction of the beam with elements of the target. In the present case the resonant reaction $^{1}H(^{15}N^{2+},\alpha\gamma)^{12}C$ is used to profile the hydrogen concentration. FTIR measures the absorption spectrum of an incident infrared radiation; the spectrum informs on the nature of the chemical bonds of the specimen compounds and is used for identification of compounds in very small sample specimens. It is shown that the solution pH is of great importance, as is the presence of polluting species such as SO_2 in the weathering atmosphere. Particularly spectacular is the AFM study illustrated in Fig. 13 (AFM has been presented in section 3.2). In the present case, the method is used to follow the evolution of a cleaned model glass surface in real time, under an artificial polluted atmosphere.

The reported features are very similar to those observed by the same method on an historical weathered stained glass window (Cathedral of Leòn, 13th century, Spain, Fig. 14).[17] The authors use AFM in ''non-contact mode'', so the surface is completely preserved from possible deterioration by the AFM tip during measurement.

The problem of the conservation of historical glass, especially medieval stained glass windows, against atmospheric weathering in a polluted atmosphere is still an unsolved problem. For the moment, the adopted solution is to protect the windows with a physical transparent barrier, but research is in progress to find appropriate (transparent but sufficiently protective) surface deposits that could be applied *in situ*.

4.3 Glass surface iridescence, an intentional treatment

Glass surface iridescence is not always a consequence of its weathering in the atmosphere. It may also be an intentional artistic intention. The problem of surface analysis becomes then more a question of authentication and of knowledge of the technology, for instance for restoration purposes.[18] Iridescent Art Nouveau glass of best quality was produced around 1900 by the most famous glass manufacturers Tiffany/USA and Loetz/Austria. The iridescence of 19th and 20th century glasses is a deliberate effect achieved by spraying the hot surface with stannous chloride or by applying mixtures of different metallic salts and reheating the glass in a reducing

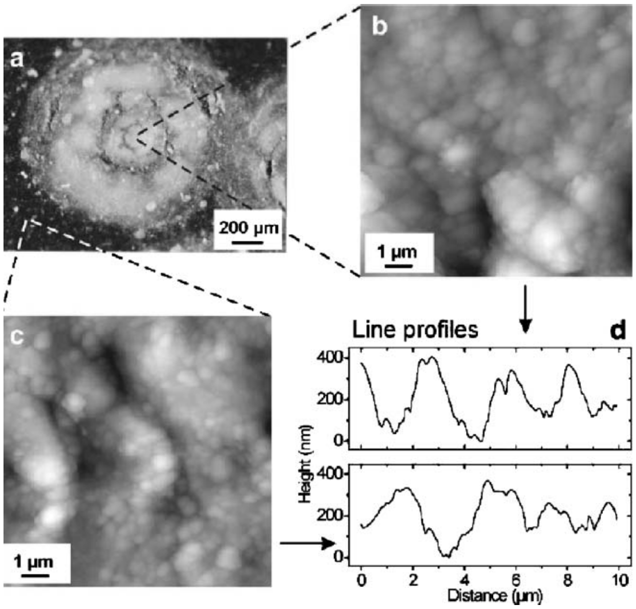

Fig. 14 AFM images and line profiles on the external surface (outside the cathedral) of a historical glass sample.[17]

oven atmosphere. This manufacturing process results in a very thin layer of SnO_2 on the glass surface. The characterisation includes then a full knowledge of the bulk and surface glass composition, and a precise measurement of the thickness and composition of the SnO_2-containing surface film. In the quoted investigation, this was achieved by combining XRF measurements for the bulk analyses and PIXE and RBS (see sections 3.2 and 3.3 for details of the methods) measurements for characterisation of the surface layer. Fig. 15 shows the result of factor analysis (a statistical analysis allowing the separation of relevant groups from a large population of results) for the differentiation of the productions of various iridescent glass objects manufacturers, and an example of an RBS spectrum which gives the characteristics of the SnO_2 surface film. The thickness of that film is of the order of 200 nm, but may be much thinner (43 nm in Fig. 15), especially for sophisticated decorations for which another glass is overlaid on the substrate glass (shining iridescent area).

5 Pigment identification and alteration

5.1 Pigment identification by μRaman spectrometry

There are several purposes behind the examination of pigments on, or removed from, paintings or manuscripts: characterisation for art history and knowledge of the artistic technique purpose; restoration, the repair of damaged areas and thus the matching to the original pigments; conservation, the care and preservation of works of art and the study of the effects of heat, light, and gaseous pollutants thereon; and dating and authentication.

The combination of XRF (detailed in section 3.2) and μRaman spectrometry (detailed in section 3.3), which may both be operated on portable instruments, has become very popular for pigment identification and analyses. XRF provides the elemental analysis and μRaman gives access to the chemical bonds of the compounds. As mentioned in section 3.3, μRaman spectroscopy[19] allows a rapid identification of the compounds at the micrometre scale; to date, it is considered as one of the most powerful methods for the study of cultural heritage artefacts. Both XRF and μRaman are non-destructive and modern equipment delivers small enough beams to analyse very small areas of an artwork. A review[19] has been devoted to the μRaman analysis of pigments and develops the advantages of that very powerful method, as well as spectacular examples of its utilisation.

In a recently published study,[20] μRaman spectroscopy has been used to identify the nature and the preservation state of the pigments present on stucco fragments (examples in Fig. 16) found in the ancient Abbassid city of Samarra, Iraq (9th century). The pigments were applied on a gypsum layer covering the plaster surface.

Individual spectra obtained from pigment crystals present in the pigments are illustrated in Fig. 17.

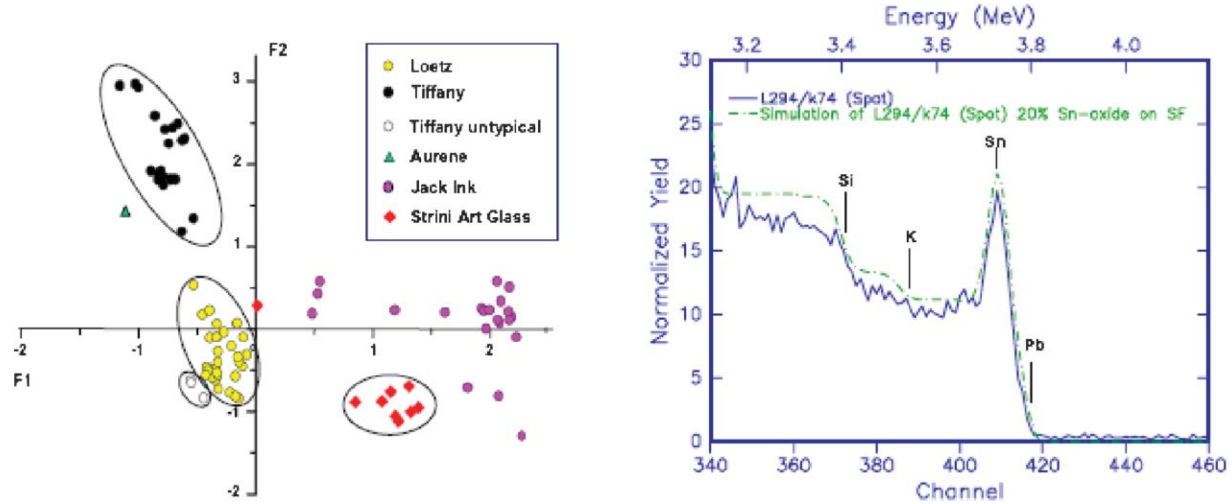

Fig. 15 Left: result of the factor analysis of the XRF data on different iridescent glasses. F1 and F2 are factors of the factor analysis, a relevant combination of complex parameters. Right: measured and simulated RBS spectrum on a Loetz glass.[18]

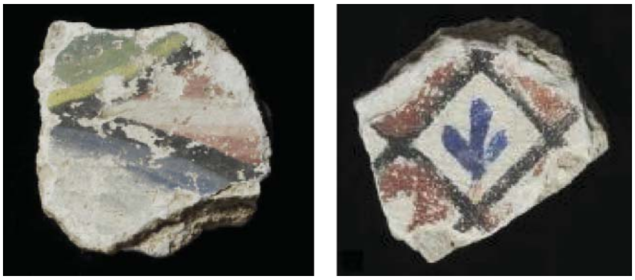

Fig. 16 Examples of decorated stucco fragments from Samarra city (V&A museum, A.43–1922 and A.56–1922).[20]

In the examples chosen here, the decoration of the fragment A.43–1922 has been fully identified, thanks to the high spatial resolution achieved in the µRaman analysis; for instance, the blue stripes are constituted of a mixture of indigo ($C_{16}H_{10}N_2O_2$) and lazurite ($Na_8[Al_6Si_60_{24}]S_n$) with some addition of red lead (Pb_3O_4) and haematite (Fe_2O_3) crystals. The same detailed description of the other colours has been done: bright green/yellow stripes (orpiment As_2S_3, carbon black and lazurite); dark green stripe (orpiment, indigo, lazurite and carbon black); red stripes (probably an organic lake plus vermilion HgS and red lead); black stripe (carbon black, with small amounts of red lead, lapis lazuli orpiment and pararealgar As_4S_4); and pink stripe (red lead, haematite and an unknown compound, with addition of lead white $2PbCO_3{\cdot}Pb(OH)_2$). The compositions of the pigments used for the fragment A.56–1922 are much simpler: lazurite for the blue pigment; vermilion for the brick red pigment; and carbon black for the black pigment.

This study is a particularly demonstrative example of the power of Raman microscopy for an individual identification of the compounds that were mixed together to obtain very subtle decorative effects. The results give important information on the painting techniques used. For example, it is interesting that different pigments were mixed to achieve deeper or more subtle colours, which resulted in a 'watercolour' effect in the fragment A.43–1922 (Fig. 16). The identification of the pigments used begs the question as to their places of origin, and points to the Abbassid empire's position at the centre of a wide network of international trade. The results have important implications also for collection management and handling recommendations, for example, with the presence of pigments containing poisonous arsenic!

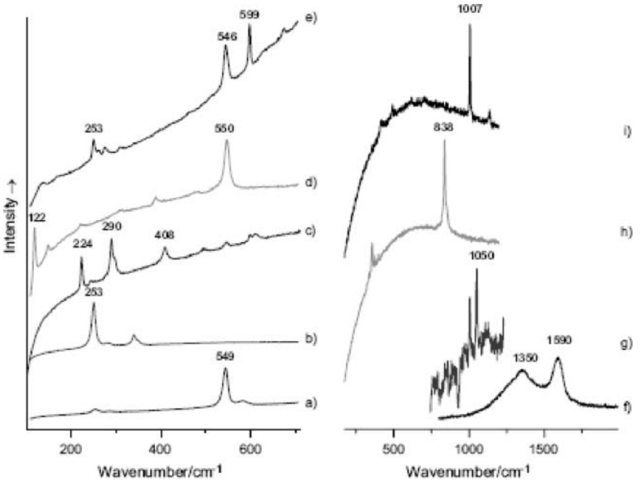

Fig. 17 Raman spectra of pigments from the stucco fragments A.56–1922 and A.43–1922: (a) lazurite, (b) vermilion, (c) haematite, (d) red lead, (e) indigo, (f) carbon black, (g) lead white and gypsum, (h) lead(II) chromate, (i) gypsum.[20]

5.2 FTIR and TXRF for pigment identification

Another powerful tool for the identification and degradation study of pigments is FTIR. As Raman spectrometry, FTIR (described in section 4.2) is sensitive to molecular bond vibrations. It has to be coupled to an elemental analysis method.

In the present example,[21] which concerns the study of the wall painting technique of a 16th century famous Albanian painter, Onoufrios, elemental analysis of the pigment samples collected on Byzantine churches is done by TXRF. TXRF is XRF conducted on a very small quantity of matter (less than 1 µg) placed on a flat substrate (Si or SiO_2) in a position of total reflection for the incident X-ray beam. FTIR, done on the same sampled very small quantities, is used for the identification of the nature of the pigments. The combination of elemental and structural analyses gives information on the artistic technique and on the alteration state of the paintings (here a wall painting). Such preliminary work is obviously necessary before starting any restoration program.

5.3. Surface XPS analysis for the study of pigment alteration

The alteration of a pigment by the environment may not be homogeneous; it starts logically from the surface. The use of surface analysis methods may be of great help to understand the mechanism of alteration and prepare conservation programs.

Altavilla and Ciliberto[22] have used XPS to characterise the chemical evolution of copper resinate pigment. Copper resinate is the name commonly given to the transparent green glazes that are coloured by copper salts of resin acids. This pigment was most commonly used in Europe in the 15th and 16th centuries, but it does not seem to be a usual feature of the palette anywhere after the end of 16th century, because its tendency to discolour was already widely known by artists of the time. The exact nature of that pigment is not well established, as some authors have shown that supposed copper resinate specimens are in fact copper oleate resulting from a reaction between copper-containing pigment probably verdigris and the oil used as a binding medium.[23] The aim here is not to take part in that discussion but to illustrate an original analysis process used to identify a mechanism of surface degradation.

Specimens are prepared by traditional methods, using linseed oil as a binder, and analyses are performed both on the surface exposed to a controlled polluted environment containing SO_2 and NO_2 and on the protected surface of the same specimen. XPS is a surface analysis method in which the kinetic energies of core shell photoelectrons, excited in the outermost surface layer (<10 nm) by means of high intensity X-ray radiation, are measured to obtain their electron binding energies. In this study, monochromatic Al Kα radiation

(1486.6 eV) was used. The energy of the photoelectrons was characteristic of the elemental species, for all elements (except H, for instance B is detected), but also of their atomic environment, *i.e.* the type of chemical bonds they are involved in. In this case, copper was in the cupric (Cu^{II}) state, and experimental precautions must be taken into account for a known risk of reduction to the Cu^{I} state by reduction under the incident X-ray beam. The photoelectron intensity is proportional to the atomic concentration of each element.

The results indeed show a strong difference between the two surfaces; XPS analysis of artificially aged models showed interesting chemical modifications. The spectrum of the external interface (paint layer–air) showed the presence of pollutant signals (S 2s, S 2p, N 1s) that were absent in the analogous spectrum recorded on the internal interface (paint layer–glass substrate) of the same sample. This result suggests that only the external surface of the layer is affected by deterioration processes and that the oil medium protects the enclosed pigment better than the protein binders, often used by the painters; tempera paintings are permeable to air pollutants and their deterioration involves the paint layer in its entirety. The high atomic concentration of copper ions on the surface (46%) strongly suggests that the green pigment is partially soluble in linseed oil. This property could explain the greater reactivity of this pigment with the external environment.

6 Organic materials

The characterisation of organic materials contained in, or constituting, cultural artefacts is a specific problem. Most organic compounds are very unstable and the observed compounds may be completely different from the original compounds present in the objects. Elemental analysis is of poor help for the identification of polymers, but is useful for the identification of specific components (section 3.1) or of given species issued from the alteration (section 3.3).

Nothing is written here about analysis of archaeological organic materials or modelling of their transformation through the ages, which are not really surface analyses problems, but full subjects by themselves. Information can be found in the work of Regert.[24]

6.1. Iron-gall ink and the preservation of old manuscripts

Library collections all over the world are affected by iron-gall ink corrosion. In all cases, visual observation proves that the first signs of ink corrosion are connected with the formation of brown edges at the ink's regions and the appearance of a brown colour on the *verso* side of the page. Following this, the brittleness of the paper increases, leading to its complete degradation. Systematic research into ink corrosion began after a conference on this subject in St Gallen (Switzerland) in 1898. The presence of transition metals began to be taken into account because transition metal ions were known to catalyse the oxidative degradation of cellulose and other organic substances present in the paper support. But paper support and ink contain a variety of ingredients, and it is clear that the chemistry of reactions leading to ink corrosion requires further investigation in order to propose effective conservation treatments.[25]

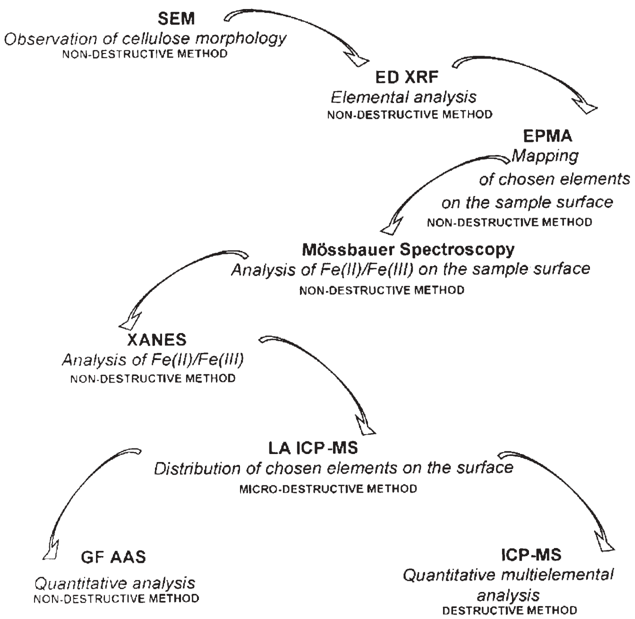

Fig. 18 Sequence of use of analytical methods for the investigation of an altered manuscript.[26]

A representative example is given by Bulska and Wagner.[26] The work is centred on a manuscript of the beginning of the 16th century entitled "*Meditationes, passionis domini nostri Iesu Christi*" (National Library of Poland, Warsaw). In the paper, the applied sequence of the use of various analytical methods is presented (Fig 18). SEM-EDS and XRF (see sections 3.1 and 3.2) are used for selecting the elements for further inspection by EPMA (EPMA is equivalent to SEM-EDS with a better quantitative accuracy, thanks to a better detection geometry and a wavelength dispersive X-ray spectrometry). LA-ICP-MS, mass spectrometry of the matter sputtered from a few μm diameter laser impact, gives a precise analysis of the trace impurities.

Synchrotron XANES is used to investigate the chemical state of iron, the main metal component of gallic inks. The basic process of X-ray absorption is the excitation of electrons from a deep core level of a selected atom, by the absorption of photons. XANES spectroscopy incorporates the structure of the spectra below as well as above the ionisation potential. Spectral features below the ionisation potential are attributed to transitions of the excited electron to non-occupied molecular orbitals. The region above the ionisation potential is dominated by multiple scattering effects of the outgoing electron wave. This part of the spectrum contains information on the geometrical arrangement of the atoms around the absorbing atom and the electronic structure of this atom. The most important observation is that energy of the absorption edge depends on the valence state of the investigated compound. μXANES measurements under synchrotron radiation may be executed with a lateral resolution of 30–40 μm or less in order to determine the local environment of iron. To extract quantitative information reference samples are used.

The authors find that around the outside borders of the written area, iron is predominantly present as Fe^{III}, while in the inner part more Fe^{II} is present. The Fe^{II} ions originate from iron sulfate, which was always used as a basic component of iron-gall ink. When ink contained an excess of iron not bound in coloured complexes with tannins, iron ions can partially oxidise to form insoluble hydrated Fe^{III} oxide (rust). In this form the iron is catalytically inactive. Paper and iron-gall ink contain many substances that can reduce the Fe^{III} ions back to the Fe^{II} form. Fe^{II} ions catalyse the oxidation degradation of cellulose by the formation of hydroxyl radical ($HO^{\bullet}$) from hydrogen peroxide. Hydrogen peroxide is formed during the reduction of molecular oxygen by Fe^{II} ions.

In order to diminish the unwanted destruction of cellulose, a conservation strategy for the paper should include not only a de-acidification, but also a deactivation of the non-bound iron ions. But, it was found that metal-catalysed oxidation can take place independently from acid hydrolysis and therefore that a special conservation strategy needs to be developed for iron-gall ink corrosion.

The degradation of paper documents associated with iron-gall ink has also been investigated using in-air PIXE[27] (described in section 3.3). The possible analytical problems such as weight concentrations of elements in paper, inhomogeneity in lateral distribution, and paper surface roughness are discussed.

6.2 Ageing and preservation of paper

Cellulose is the main component of paper. Its degradation occurs as a result of internal or external factors, such as intrinsic acidity of the paper or storage in an unsuitable place. Degraded papers show an evident fragility and a yellowing, which compromises the legibility of the text. The main degradation mechanisms involved are oxidation and hydrolysis. The first causes the formation of double bonds on the anhydroglucose ring and of carbonyl groups, which can be further oxidised to carboxylic groups. Oxidation can lead both to the breaking of the cellulose chain (depolymerisation) or to the opening of the rings, thus making alkaline or acidic attacks on the macromolecule easier. Hydrolysis breaks the chain and causes a fragmentation of the structure, and may occur both in acidic and alkaline environments, but at room temperature only the acidic process can take place.

Piantanida *et al.*[28] report a study of these processes on a cotton cellulose paper, using chemical analysis, AFM (described in section 3.2) and spectrophotometry (described in section 4.1) using an accelerated ageing procedure in a climatic chamber (80 °C, 65% relative humidity). The increased formation of $C=O$ double bonds and of carboxyl radicals is quantified and correlated to the surface evolution followed by AFM and spectrophotometry. The latter allows the yellowing of the paper to be followed quantitatively by the increase of the CIE b* (yellow) coordinate (*cf.* section 4.1) and AFM quantifies the progressive increase of the surface corrugation.

In paper-supported works of art, the colonisation of cellulose substrate by specific groups of micro-organisms often represents something more than a mere aesthetic problem. In a recent study, the same research group[29] used AFM to observe the degradation of cellulose fibres in paper by a filamentous fungus, *Aspergillus terreus*, known to be responsible for damage to paper. Images obtained are compared with artificially deteriorated samples aged for 49 days in a climate chamber at 80 °C, a reference sample and a naturally bio-deteriorated paper from a 1568 letter from Innocenzo Coret. It is shown that original degraded library objects cannot be easily modelled using a single sample (Fig. 19). When the deterioration process is applied by laboratory experiments on the same kind of paper as the historical manuscript, the surface roughness deviation is not affected by experimental uncertainty; on the contrary, a major deviation was found in the roughness of stain samples taken from the naturally bio-deteriorated historic manuscript.

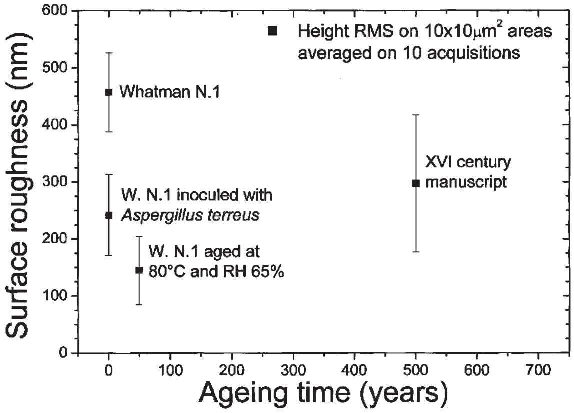

Fig. 19 Comparison of surface roughness parameter of different papers.[29]

In another study[30] a protection treatment is proposed, based on plasma enhanced vapour deposition (PECVD) under hexamethyldisiloxane of a thin transparent film that enhances the mechanical strength of the paper and brings a somewhat efficient protection against humidity (see section 3.2 for another application of that kind of preventive treatment).

6.3. Wood preservation: the preservation of the *Vasa* warship

A famous application of conservation policy research is the problem of the long term conservation of the *Vasa*.[31] Sweden's famous warship, *Vasa*, capsized on her maiden voyage in 1628 and remained on the bottom of Stockholm harbour for 333 years. She provides invaluable information about the society and the technology of the 17th century (Fig. 20).

Fortunately, she remains largely intact. Many of the sculptures had fallen into the silt, saving them from decay and erosion. The oak structure was generally in good condition, but long-term conservation of the waterlogged wood required careful analyses, proper chemical evaluation and treatment. Poly(ethylene glycol) (PEG) was chosen to replace water and prevent cracking when drying the waterlogged wood. During the spray treatment period, a mixture of borax, $NA_2B_4O_7\cdot10H_2O$ and boric acid, $B(OH)_3$ was dissolved in the PEG as a fungicide. In 1988, *Vasa* was transferred to the Vasa Museum. The excess PEG was removed from the surface using hot air blowers. Preservation would consist of periodic cleaning and monitoring of the climate to assure optimum temperature and humidity. But, the wet summer of 2000, combined with a record number of visitors, caused the room humidity within the ship hall to exceed a level of 65%. Yellow

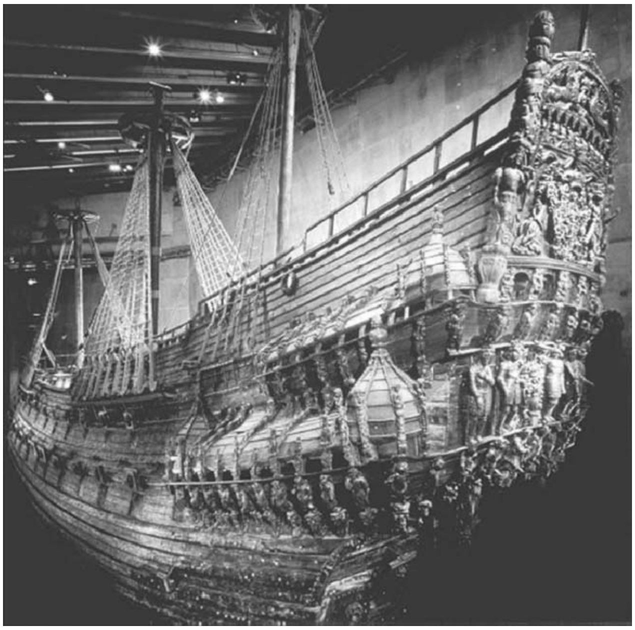

Fig. 20 The *Vasa* in the Vasa museum (© Hans Hammarskio and the Vasa Museum, Stockholm, Sweden).[31]

and white precipitates were observed on the surfaces of artefacts. These areas showed pH levels lower than 3 (measured with wet pH-indicator paper). These precipitates were identified by XRD (section 3.1): hydrated iron sulfates; rozenite ($Fe^{II}SO_4\cdot4H_2O$); melanterite (($Fe^{II}SO_4\cdot7H_2O$); natrojarosite ($NaFe^{III}{}_3(SO_4)_2(OH)_6$); gypsum ($CaSO_4\cdot2H_2O$); and elemental sulfur (orthorhombic S_8).

Profiles of sulfur concentrations along the wood were determined by high-resolution X-ray fluorescence (see section 3.2). The X-ray fluorescence was excited by means of a focused CuKα X-ray beam and an energy dispersive solid state X-ray detector provided $\sim$0.5 mm resolution and an analytical depth in the wood of about 0.1 mm. Well chosen standard samples were scanned to achieve quantitative calibration. Specification of the sulfur compounds was possible by sulfur K-edge XANES (presented in section 6.1).

XPS was used (presented in section 5.3), which confirmed the three sulfur components: sulfate peak; sulfoxide peak; and reduced sulfur, consistent with the XANES results.

A high accumulation, in some cases exceeding 10% S by mass, occurs in the outer first centimetres (Fig. 21). But the analyses indicated that, where high sulfur levels are found, there are correspondingly high levels of iron. Iron is a strong catalyst for many chemical reactions and clearly plays a role here; *Vasa*'s wood has a high iron content (nails, cannon balls, *etc.*). But where did the sulfur come from? For hundreds of years the waters of Stockholm harbour were polluted by sulfate-rich natural waste. In this largely anaerobic environment, sulfur-reducing bacteria metabolised this sewage, utilising the oxygen from the sulfate ion (the SO_4^- concentration is about 0.3 g l^{-1} in the Baltic Sea) to produce dissolved hydrogen sulfite. This substance is toxic for many organisms and this, combined with the low oxygen level, contributed to *Vasa*'s good preservation. Note also that the low water temperature (between 0 °C and 5 °C) slowed the chemical and biological deterioration processes. When the ship was raised, the conditions were optimal to create sulfuric acid in the wood.

The investigation went further towards understanding the consequences of the presence of such high amounts of deleterious compounds on the future degradation of the *Vasa* wood parts. A detailed analysis has been performed to understand the microscopic mechanisms of fixation of the acid and of the alteration of the wood microstructure. This led to a considerable amount of published work and to the creation of an international project "preserve the *Vasa*", whose working policy and orientation trends are detailed by Hocker.[32]

7 Conclusion

"Conservation science", a questionable neologism proposed recently[33] by cultural heritage specialists to designate the process that starts from the full characterisation of artefacts and intends to lead to a conservation policy for those artefacts, including restoration and preventive conservation, is a complex and multidisciplinary science. In order to conduct

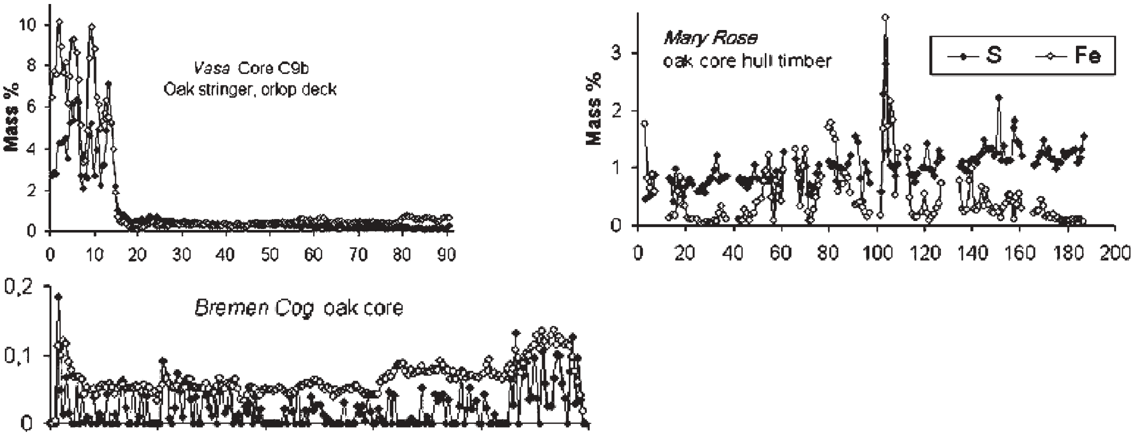

Fig. 21 X-Ray fluorescence high resolution line scans (depth in mm) of total sulfur and iron in cores of different ships.[31]

the best possible conservation of the objects, the research process leading to as complete a knowledge of their constitution and properties as possible cannot be avoided.

In that process, material surface science plays a key role, because most cultural heritage goods are accessible to characterisation only through non-destructive analyses of their surfaces. The cooperation between surface scientists, art historians, historians of techniques, museum curators, archaeologists, conservators and restorers is, ideally, a necessary condition for a comprehensive process to be profitable.

We hope that the examples briefly described in this paper will show that the modern characterisation tools now in the hands of surface scientists have brought cultural heritage material science to an excellent level. The consequence is not only a much better orientation for conservation, but also the inflow of invaluable information for a more complete knowledge of art and technique history, of the ancient civilisation way of life and of mankind in general.

Appendix: acronyms used in the article

AES	Auger electron spectroscopy
AFM	Atomic force microscopy
EDS	Energy dispersive (emitted X-ray) spectrometry
EPMA	Electron probe microanalysis
ERDA	Elastic recoil detection analysis
ESEM	Environmental scanning electron microscopy
EXAFS	Energy X-ray absorption fine structures
FIB	Fast ion bombardment
FTIR	Fourier transformed infrared absorption spectroscopy
IBA	Ion beam analyses
GXRD	Grazing angle X-ray diffraction
ICP-AES	Inductive coupled plasma-atomic emission spectrometry
ICP-MS	Inductive coupled plasma-mass spectrometry
LA-MS	Laser ablation mass spectrometry
NMR	Nuclear magnetic resonance
NRA	Nuclear reaction analysis
PIXE	Particle-induced X-ray emission
RBS	Rutherford backscattering spectrometry
SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectrometry
TEM	Transmission electron microscopy
ToF-SIMS	Time-of-flight secondary ion mass spectrometry
XANES	X-Ray absorption near edge structure
TXRF	Total reflection X-ray fluorescence
XPS	X-Ray induced photoelectron spectrometry
XRD & μXRD	X-Ray diffraction and micro-X-ray diffraction
XRF & μXRF	X-Ray fluorescence and micro-X-ray fluorescence

References

1 *Non-destructive Microanalysis of Cultural Heritage Materials*, ed. K. Janssens and R. Van Grieken, *Comprehensive Analytical Chemistry*, vol. XLII, Elsevier, Amsterdam, 2004, and references cited therein.

2 R. Bertholon, *PhD thesis*, Paris I, 2000; R. Bertholon, *La Revue de Métallurgie-CIT/Science et Génie des Matériaux*, EDP Science, Paris, September 2001, pp. 817–823; R. Bertholon, Archaeological metal artefacts and conservation issues: long term corrosion studies, in *Corrosion of Metallic Heritage Artefacts: Investigation, Conservation and Prediction of Long Term Behaviour (European Federation of Corrosion 48)*, ed. P. Dillmann, G. Beranger, P. Piccardo and H. Matthiessen, Woodhead Publishing, Cambridge, UK, 2007.

3 D. Scott, in *Non-destructive Microanalysis of Cultural Heritage Materials*, ed. K. Janssens, R. Van Grieken, *Comprehensive Analytical Chemistry*, vol. XLII, Elsevier, Amsterdam, 2004, pp. 465–492.

4 E. Angelini, S. Grassini, G. Solorzano, G. Do Nascimento Campos and T. de Caro, *Appl. Phys. A: Mater. Sci. Process.*, 2006, **83**, 485.

5 P. Craddok and A. Giumla-Mair, in *Metal Plating and Patination*, ed. S. La Niece and P. Craddok, Butterworth, London, 1993, pp. 101–127.

6 F. Mathis, *PhD thesis*, Paris XI, 2005; F. Mathis, J. Salomon, S. Pagès-Camagna, M. Dubus, D. Robcis, M. Aucouturier, S. Descamps and E. Delange, Corrosion patina or international patina: contribution of non-destructive analyses to the surface study of copper based archaeological objects, in *Corrosion of Metallic Heritage Artefacts: Investigation, Conservation and Prediction of Long Term Behaviour (European Federation of Corrosion 48)*, ed. P. Dillmann, G. Beranger, P. Piccardo and H. Matthiessen, Woodhead Publishing, Cambridge, UK, 2007.

7 T. Calligaro, J.-C. Dran and J. Salomon, in *Non-destructive Microanalysis of Cultural Heritage Materials*, ed. K. Janssens and R. Van Grieken, *Comprehensive Analytical Chemistry*, vol. XLII, Elsevier, Amsterdam, 2004, pp. 227–276.

8 D. Bougarit and B. Mille, *Meas. Sci. Technol.*, 2003, **14**, 1538.

9 M. Dubus, M. Aucouturier, S. Colinart, J.-C. Dran, M. Gunn, B. Moignard, J. Salomon, P. Walter, I. Colson, A.-M. Laurent and M. Leroy, in *ICOM Committee for Conservation 13th Triennial Meeting, Rio de Janeiro*, Earthscan, London, 2002, pp. 851–859.

10 A. Caiger-Smith, *Lustre Pottery: Technique, Tradition and Innovation in Islam and the Western World*, Faber and Faber, London, UK, 1985.

11 J. Perez-Arantegui, J. Molera, J. Larrea, A. Pradell, T. Vendrell-Saz, I. Borgia, B. G. Brunetti, F. Cariati, P. Fermo, M. Mellini, A. Sgamelotti and C. Viti, *J. Am. Ceram. Soc.*, 2001, **84**(2), 442, and references cited therein.

12 D. Hélary, *PhD thesis*, Ecole des Mines de Paris, 2003; E. Darque-Ceretti, D. Hèlary, A. Bouquillon and M. Aucouturier, *Surf. Eng.*, 2005, **21**(5–6), 352.

13 D. Hélary, E. Darque-Ceretti and M. Aucouturier, *J. Am. Ceram. Soc.*, 2005, **88**(11), 3218; P. Fredricks, D. Hélary, D. Schryvers and E. Darque-Ceretti, *Appl. Phys. A: Mater. Sci. Process.*, 2004, **79**, 283.

14 D. Chabanne, M. Aucouturier, A. Bouquillon and E. Darque-Ceretti, *Matériaux 2006*, Dijon, France, Nov. 2006, Fédération Française des Matériaux, Paris, CD-ROM available, and references cited therein.

15 M. Schreiner, in *Non-destructive Microanalysis of Cultural Heritage Materials*, ed. K. Janssens and R. Van Grieken, *Comprehensive Analytical Chemistry*, vol. XLII, Elsevier, Amsterdam, 2004, pp. 713–754, and references cited therein.

16 E. Darque-Ceretti and M. Aucouturier, in *Non-destructive Microanalysis of Cultural Heritage Materials*, ed. K. Janssens and R. Van Grieken, *Comprehensive Analytical Chemistry*, vol. XLII, Elsevier, Amsterdam, 2004, pp. 397–461, and references cited therein.

17 M. Garcias-Heras, N. Carmona, A. Ruiz-Cone, P. Sánchez-Soto and J.J. Benítez, *Mater. Charact.*, 2005, **55**, 272.

18 D. Jembrich-Simbürger, C. Neelmeijer, M. Mäder and M. Schreiner, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2004, **226**, 119.

19 *Raman Spectroscopy in Archaeology and Art History*, *Analytical Spectroscopy Monographs*, ed. H. G. M. Edwards and J. M. Chalmers, Royal Society of Chemistry, Cambridge, 2005, and references cited therein; G. D. Smith and R. J. H. Clark, *J. Archaeol. Sci.*, 2004, **31**, 1137, and references cited therein.

20 L. Burgio, R. J. H. Clark and M. Rosser-Owen, *J. Archaeol. Sci.*, 2007, **34**, 756.

21 E. Pavlidou, M. Arapi, T. Zorba, M. Anastasiou, N. Civici, F. Stamati and K. M. Paraskevopoulos, *Appl. Phys. A: Mater. Sci. Process.*, 2006, **83**, 709.

22 C. Altavilla and E. Ciliberto, *Appl. Phys. A: Mater. Sci. Process.*, 2006, **83**, 699.

23 M. H. van Eikema Hommes, in *Art of the Past: Sources and Reconstructions, Proceedings of the First Symposium of Art Technological Source Research Study Group*, ed. M. Clarke, J. H. Townsend and A. Stijman, Archetype, London, 2005, p.16; K. J. van den Berg, M. H. van Ekeima Hommes, K. M. Groen, J. J. Boon and B. H. Berrie, in *Art et Chimie, la Couleur. Actes du Congrès*, ed. J. Goupy and J.-P. Mohen, 2000, CNRS Editions, Paris, pp. 18–21.

24 M. Regert, *J. Chromatogr., A*, 2006, **1101**, 245, and references cited therein.

25 The ink corrosion web site can be found at http://www.knaw.nl/ecpa/ink/ink_chemical.html, and references cited therein.

26 E. Bulska and B. Wagner, in *Non-destructive Microanalysis of Cultural Heritage Materials*, ed. K. Janssens and R. Van Grieken, *Comprehensive Analytical Chemistry*, vol. XLII, Elsevier, Amsterdam, 2004, pp. 755–788.

27 M. Budnar, M. Uršič, J. Simčič, P. Pelicon, J. Kolar, V. S. Šelih and M. Strlič, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2006, **243**, 407.

28 G. Piantanida, M. Bicchieri and C. Coluzza, *Polymer*, 2005, **46**, 12313.

29 G. Piantanida, F. Pinzari, M. Montanari, M. Bicchieri and C. Coluzza, *Macromol. Symp.*, 2006, **238**, 92.

30 E. Vassallo, L. Laguardia, D. Ricci and G. Bonizzoni, *Macromol. Symp.*, 2006, **238**, 46.

31 Y. Fors and M. Sandström, *Chem. Soc. Rev.*, 2006, **35**, 399, and references cited therein.

32 E. Hocker, *Macromol. Symp.*, 2006, **238**, 16, and references cited therein.

33 J. Townsend, *Macromol. Symp.*, 2006, **238**, 1.