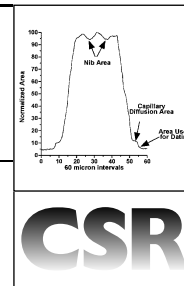


Probing archaeological and artistic solid materials by spatially resolved analytical techniques



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The study of ancient works-of-art and archaeological remains requires the use of analytical methods which minimise the impact on the integrity of the object. Spatially resolved analytical methods have significantly enhanced our capacity to study ancient material since they cause minimal and at times no damage to the studied object. They have also amplified the range of analytical information we can extract from ancient and valuable objects. Here we provide an overview of the recent achievements in the knowledge of the past obtained thanks to the use of a variety of spatially resolved analytical methods.

1 Introduction

The analytical methods used in the study of antiquities go back to the 18th century. Eminent scientists such as Humphry Davy, Jöns Jakob Berzelius, Michael Faraday, Marcellin Berthelot, Friedrich August von Kekulé and Wilhelm Conrad Röntgen turned their attention to ancient coins, glasses, pigments, pottery and other remnants of the past during the course of their studies. Similar investigations continued throughout the 19th century thanks to a number of other investigators, most of them operating in isolation.

The use of scientific examination in order to shed light on the past was greatly fostered when major museums began to establish laboratories for that purpose on their premises. After a scientific laboratory was established in 1888 at the Königlichen Museum in Berlin the director Friedrich Rathgen provided the first manual dealing with practical procedures for the conservation and restoration of antiquities.¹ This handbook remained for many years the only collected scientific documentation in the field. It was in 1920, as a direct result of the First World War, that one of the leading laboratories in the field was established at the British Museum. The discovery of the alterations suffered by many of the objects stored in 1918 in the Holborn Post Office tunnel as protection against possible war damage² moved the Trustees to invite Alexander Scott to carry out an investigation. On the basis of his report an emergency laboratory was set up in 1920 within the precincts of the British Museum. At this time Alexander Scott was aged 70 and was a senior fellow of the Royal Society, Superintendent of the Davy Faraday Laboratory of the Royal Institution and President of the Chemical Society. His interests, ranging from sciences to arts, led to the systematic application of scientific methods to the study of ancient objects held in museums.³

The pioneering approach developed in museum science laboratories was followed by the involvement of university laboratories which ensured the continuous development of new analytical methodologies for the investigation of remnants of

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the past. In spite of this continuous evolution, only in the past four decades has the use of advanced analytical instrumentation, together with the increased knowledge of statistical methods for the elaboration of coherent data sets, established a fundamental link between instrumental analytical chemistry, art and archaeology. The opening in 1955 of the Research Laboratory for Archaeology and the History of Art at Oxford University was certainly a starting point for this process. Today, science departments are normally active within the major museums, while departments and institutes devoted to studies of relevance to science applied to art and archaeology are present in most of the world's university institutions. The wider use of scientific techniques to examine ancient artefacts has allowed specific sub-branches of the subject to be established. One of these, the use of spatially resolved techniques, is the matter of this overview where a selection of specific case studies is provided.

All scientists involved in studies concerning works-of-art or samples of archaeological interest will recognise how important it is to make an appropriate selection of the analytical method to be used in their studies. The main questions raised usually concern how the proposed analytical procedure will affect the object to be examined in its integrity. From this point of view, only those techniques which do not alter the integrity and appearance of artistic and/or archaeological objects are eligible as "ideal" techniques. Techniques which operate *in situ*, making sample taking unnecessary, come close to this ideal.

In the attempt to find a balance between the requirements of scientific methods and the need to maintain the integrity of the object under study, the only alternatives to *in situ* analysis require the object itself to be placed in the analysing chambers of the analytical instrument or tiny fragments of samples to be scraped from its surface. The former approach cannot be applied in all cases, since only small objects such as coins, certain jewellery and statuettes are of a size and shape which will fit those of common analytical tools. The destructive approach thus remains as a last resort for the extraction of analytical information from artistic and/or archaeological samples.

Tremendous improvements have been made as regards the scope and efficiency of today's analytical instruments. This has led to the development of new analytical methodologies that satisfy specific requirements to a greater degree such as micro-destructiveness or non-destructiveness of the sample to be analysed. A wider range of information is now available and the greater sensitivity and reproducibility of analyses is thus ensured. In this context, the use of spatially resolved analytical techniques have provided new opportunities for micro-destructive and, at times, completely non-destructive analyses, thus opening up new diagnostic approaches for the study of samples of artistic and/or archaeological importance.

The novel aspect of spatial resolution is to image the distribution of elements/compounds across the sample surface. The *in situ* analysis of microscopic areas of the work-of-art may be accomplished by spatial resolution, thereby allowing the extraction of a wide range of valuable analytical information that can also be imaged into 2D or 3D graphics. Spatial resolution also renders it possible to analyse tiny fragments of samples scraped from the object of interest with minimal damage to the artefact itself. Such facilities have often allowed scientists to overcome the reluctance of art curators to provide access to important artistic and archaeological material. Science has thus contributed to the accumulation of a wealth of fundamental information about the customs, technical and economical achievements and artistic skills of ancient populations.

The information provided by analytical studies of works-of-art and archaeological remains has often been of a scattered nature. It is only recently that the wider availability of specialised journals, the establishment of data banks and the more systematic organisation of research activities in the field

have allowed the production of comprehensive accounts concerning the use of analytical methods in art and archaeology. Such efforts have reinforced links between museums, archaeological boards and institutions and university science departments. This paper aims to help consolidate such links by providing an overview of recent achievements in the knowledge of the past where results were obtained thanks to the use of a variety of spatially resolved analytical methods. The scope of this journal does not permit a comprehensive account of the field, thus here a selection of specific case studies will be provided. Full discussion of basic issues concerning chemistry, art and archaeology can be found elsewhere.^{4,5} For more detailed descriptions of the use of specific techniques in the field of interest suggestions will be supplied for further reading.

We hope that the present overview will act as springboard for further reading and that it will stimulate others to enter this fascinating area of research.

2 Spatial resolution

Spatial resolution defines the level of spatial detail depicted in an image. It indicates how fine a detail can be detected in terms of distance in space and may be described as measuring the smallness of objects against a background that may be distinguished as separate entities in an image. This definition, which traditionally deals with image reproduction, has also been recently applied to the spectroscopic analytical field. In fact, the ability to extract and separate analytical information from regions of a sample with a diameter in the range of microns/submicrons has led to the development of a new class of analytical techniques. Most of these techniques involve probing the sample by exposing it to a flux of particles (photons, electrons, ions, neutrals) and simultaneously measuring the energy distribution of a specific class of emitted or scattered particles. The particles revealed may differ from those used to irradiate the sample. Moreover, different attributes (wave vector, equivalent momentum *etc.* . . .) may be revealed in place of/together with the energy of the selected particles. Fig. 1 shows the probed and detected particles involved in the techniques discussed. The acronym and the typical spatial resolution of each technique is also shown.

The ability to spatially resolve analytical data can be used to collect information from a specific region of the sample with an area usually in the range of μm^2 —*localised spectroscopy*—or to investigate the spatial distribution of an analytical entity within the sample matrix—*spectroscopic imaging*. Both methods have been used to study works-of-art and archaeological objects. Nevertheless, localised spectroscopy has mostly been used for such studies. In the latter cases, spatial resolution is a direct consequence of the ability to focus the incoming and/or the revealed beam particles. Charged particles (ions, protons and electrons) are easily focused and deflected by means of electrostatic and magnetic lenses. Techniques such as auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) can thus be considered as *inherently spatially resolved* spectroscopic methods. In contrast, techniques involving the use of photons have a lower spatial resolution due to the difficulties found in focalising optical beams at the submicron level. For such techniques the ultimate achievable spatial resolution is fixed by the diffraction generated when the diameter of the slits used to collimate the incoming beam is reduced to the same magnitude as the wavelength of the selected radiation. FT-IR microspectroscopy and micro-Raman spectroscopy are two of the analytical techniques with a diffraction limited spatial resolution discussed in this paper.

Near field scanning optical microscopy (NSOM; also known as SNOM) has recently been proposed as an optical technique

whose spatial resolution can overcome the diffraction limit.⁶ The coupling of this optical technique with Raman or FT-IR spectrometers can produce spectra with a spatial resolution down to 100–200 nm. Unfortunately, to the best of our knowledge, there are as yet no applications of this technique to the field discussed.

Spectroscopic imaging produces images where a spectral signature is associated with each spatial resolution element, *i.e.* pixel. The spectral signature can be obtained from a variety of phenomena such as the emission of X-ray fluorescence radiation, infrared radiation, photoelectrons, Auger electrons, secondary ions or Raman scattered radiation. A spectral imager provides data in the form of a three-dimensional cube with two spatial dimensions and a third spectral dimension. The third dimension is often shown as a grey scale or as false colour representations.

Imaging experiments usually employ some form of two basic acquisition strategies—direct imaging or mapping. Direct imaging has become more popular since the availability of extremely sensitive two-dimensional array detectors [*e.g.*, charge-coupled devices (CCDs)]. The surface of these detectors is covered with a grid of microscopic light-sensitive elements that generate voltage in proportion to the amount of light they receive. Imaging is accomplished by bombarding the sample with a defocused beam and collecting the emitted radiation by means of a two-dimensional array detector positioned on the focal plane of the optical system. The detector reconstructs the spatial distribution of the emitted radiation whose energy is selected by means of discrete or tunable filters. Modern CCDs are sensitive to a wide spectrum of radiation ranging from the visible to X-rays. The positioning of fluorescent screens which can convert the gained signal into visible light in front of a CCD also make it possible to detect particles (*e.g.*, electrons and ions), thus expanding the potential of direct imaging.

Mapping involves a different acquisition strategy based on the collection of a spectrum from each spatial location of the area to be imaged. The image is reconstructed by associating each spatial location to the analytical information provided by the spectrum. Mapping can be achieved in the dynamic or microprobe mode. Dynamic mapping involves the sequential detection of the spectrum, as either the incoming beam or the sample is scanned. In the latter case lower spatial resolution is achieved. It differs from the microprobe mode since the latter is accomplished through point-by-point spectrum acquisition. It is mentioned here to highlight that sample scanning is sometime used to map large works-of-art.

Each of the above mentioned imaging methods suffers drawbacks which should be properly evaluated. If compared to other methods, microprobe imaging often results in longer acquisition times thus assuring good sensitivity. The dynamic mode provides good resolution and complete sample area coverage, but at the cost of lower sensitivity. Direct imaging is

often the best compromise between speed of imaging, sensitivity and spatial resolution. It is, however, limited as regards the size of the region to be analysed. In some cases the area can be expanded but this significantly affects data collection efficiency.

A variety of other imaging methods with both direct imaging and mapping features have also been tested. Line scanning is one of these. It is mostly used for X-ray fluorescence, Raman imaging and magnetic resonance imaging. In this method the primary beam is masked to produce a line-shaped interaction area on the specimen. By line-scanning the sample a variety of spectral features can be acquired. These can be imaged using two-dimensional detectors or by mathematically decoding the collected data.

3 Spatially resolving photons: X-rays

X-rays, first described by Röntgen in 1895, have been used in the study of archaeological and artistic artefacts since 1897 when a painting by the German painter Albrecht Dürer (1471–1528) was irradiated in order to find his signature. Similar approaches have been developed throughout this century, and radiography, even in its most highly developed forms such as computer tomography, is used routinely in modern conservation laboratories. Here, however, attention will be paid to the most typical analytical side of X-ray use. X-rays emitted from atoms by fluorescence carry elemental information according to the law described by Moseley in 1912. Moseley found that the atomic number of the emitting atom and the energy of the emitted X-rays were proportional. Each element thus emits a characteristic X-ray spectrum. This fact has been used to investigate solid materials by obtaining qualitative and quantitative information for most of the elements of the periodic table. However, the difficulty met in detecting light elements such as C, N and O coupled with the fact that this method cannot provide molecular information make it unsuitable for the study of organic material.

Experimental set-ups can be categorised according to the way in which X-rays are generated and how the emitted radiation is energetically selected. X-ray fluorescence (XRF) is involved wherever high energy radiation is used to irradiate the sample; X-ray emission is, in contrast, involved when charged particles such as electrons, protons or ions are used as the bombarding beam. The emitted radiation is wavelength dispersed (WD) according to Bragg's law by means of a suitable crystal which is sequentially tilted towards or away from the beam or is energy dispersed (ED) by means of solid state lithium-drifted [Si(Li)] detectors. The use of a collimated X-ray beam makes it possible to direct the incoming beam at an extremely low glancing angle ($<0.1^\circ$) so as to interact with the surface of the sample alone.

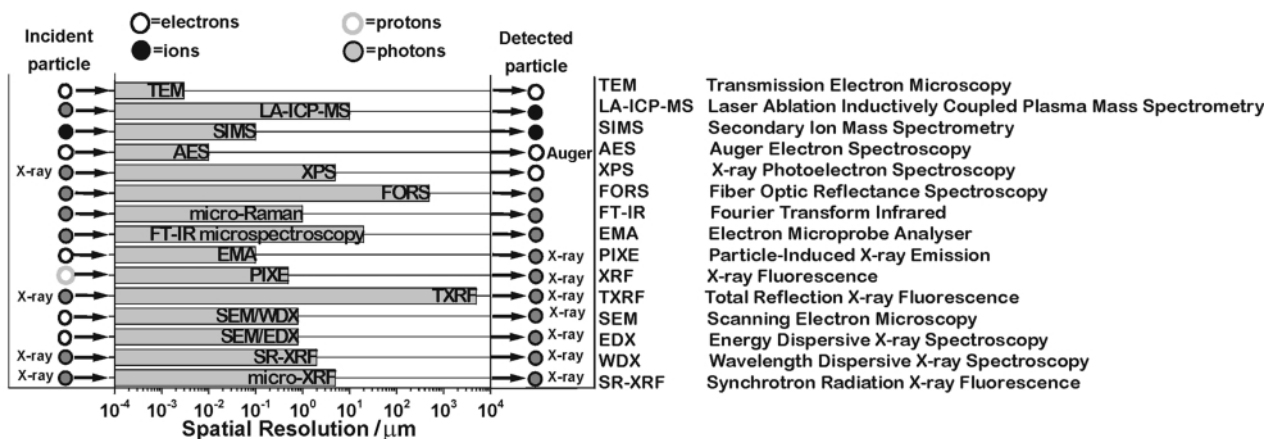


Fig. 1 Typical spatial resolution of a variety of analytical techniques. The probed and detected particles are also shown.

Total Reflection X-ray Fluorescence spectroscopy (TXRF) is attained through the collection of the characteristic fluorescent radiation.

X-ray fluorescence (XRF) has been a popular technique for the chemical analysis of archaeological and artistic artefacts since the early 1960s. At that time an enthusiastic “Milli-probe” was used to indicate a class of instruments able to reduce the size of the analysed area down to a couple of millimetres.⁷ Modern micro-XRF spectrometers provide spatial resolution in the range of 5–10 μm and are suitable for mapping experiments.⁸ The potential of direct imaging has also been demonstrated.⁹ Moreover, the use of synchrotron radiation has led to improvements both in intensity and the beam diameter of the stimulating radiation, thus reducing the achievable lateral resolution to 2–5 μm (SR-XRF).⁸ It is finally necessary to acknowledge the fundamental contribution to our knowledge of the ancient world provided by the more widely available electron microscopes [mostly scanning electron microscope (SEM) and transmission electron microscope (TEM)] which are equipped with Si(Li) detectors to provide EDX systems.

Particle-induced X-ray emission (PIXE) has several advantages to offer in the spatially resolved elemental analysis of archaeological and artistic artefacts. When using PIXE, incident particles (light ions or protons) can be more easily focused and sensitivity is greater (up to 10 ppm for most elements) in comparison with XRF. This has ensured its rapid gain in popularity since the 1970s. Modern equipment allows us to analyse solid objects non-destructively with a spatial resolution of a few hundred nanometers. Moreover, PIXE can be used to work in air (in external beam mode), thus enabling the *in situ* analysis of large or fragile objects with no need for sampling or vacuum use. The cost of an ion accelerator set-up (incident ions are usually accelerated to an energy of 2.5–5 MeV) prevents this technique from being widely available. Nevertheless, the advantages derived have prompted the Research Laboratory of the Museums of France in Paris to produce an external beam facility with a beam diameter of 10 μm specifically for use in research of interest for archaeology and art.

The potential of X-ray fluorescence and emission techniques in studies with archaeological and/or conservation purposes is demonstrated by the ever-widening range of application fields (Fig. 2). Ancient coins, pottery, stones, paintings, glasses, bones

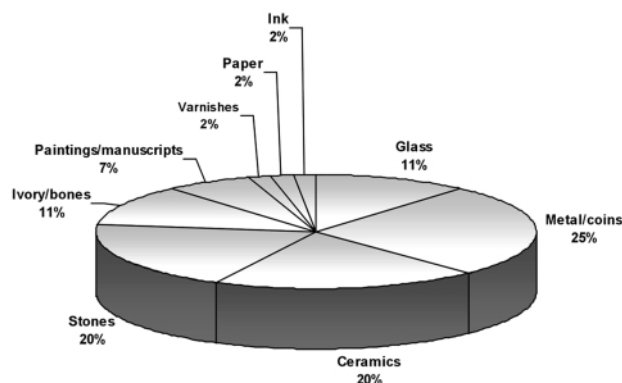


Fig. 2 Different XRF application fields and their relative importance as revealed in a literature search covering a period 1995–1998. Reproduced with permission from L. Moens, A. von Bohlen and P. Vandenneele, in *Modern Analytical Methods in Art and Archaeology*, ed. E. Ciliberto and G. Spoto, Copyright 2000, John Wiley & Sons, Inc., New York.

and manuscripts are widely studied by means of such methods.¹⁰ For example, the use of X-ray fluorescence and emission techniques made it possible to solve questions of relevance for the restoration of the *lunetta* of an important Sicilian Renaissance church.¹¹ The methods have also shed light on the sophisticated chemical technology that the ancient Egyptians used to produce make-up powders,¹² and have made it possible

to identify the chemical composition of large stone-like slabs in Mesopotamia. These were obtained in around 2000 B.C. by heating a significant quantity of silt at about 1200 °C and their chemical composition differs from that of basalt stone.¹³ The almost totally undestructive elemental characterisation of inorganic pigments used in paintings through TXRF has recently been demonstrated.¹⁰ The pigments were sampled from the painting using a cotton wool bud which was then successively analysed by TXRF.

A drawback of the use of X-ray fluorescence and emission techniques concerns the X-ray induced damage of the organic components which frequently make up the complex matrix in many works-of-art or archaeological remains. Low flux, low power and short exposure time are required in such cases in order to minimise damage. Corrosion processes, which affect most of the materials ranging from glass to metal, are also to be carefully acknowledged before X-ray fluorescence and emission analysis. They certainly represent the main problem to be faced when ancient artefacts are going to be studied. The typical depth of analysis (in the range of a few microns) can in fact in itself constitute a strong limitation for the techniques based on X-ray fluorescence and emission when the composition of the outer layers of the material is altered by corrosion processes. The extracted information varies in depth according to the procedure used to produce characteristic X-rays, to the energy and the angle at which the incoming beam hits the sample surface, and to the composition of the matrix to be analysed.

3.1 Coins

Coins are among the most common artefacts found in excavations. Their composition often reflects political or economic trends in ancient societies, even if forgery is seen to have introduced changes in composition. In the past, debasement was to the king's advantage and unofficial debasement was not encouraged. Henry I seemed to hold this matter particularly to heart, since he demanded that the right hands and testicles of some 94 moneyers be cut off over the Christmas period in 1125 in England. In the Roman era the gradual debasement of coins was associated with the decline of the empire.¹⁴ The social and economic consequences of debasement are clear if we consider that in the ancient world the value of a coin was equal to the value of the precious metal it contained. Debasement was thus coupled with dramatic inflation. A 15000 % rate of inflation has been estimated to exist in the third century. Only the ‘Maximum Price’ edict issued by Diocletian in 301 A.D., which developed the reform issued in 294 A.D., stopped the further debasement of silver coins.

Coin debasement has been studied by a variety of analytical methods. Non-spatially resolved methods have been used to analyse a great number of coins, thus building-up significant parts of our knowledge of the ancient economy. Spatially resolved X-ray fluorescence and emission techniques have also played a role in the reconstruction of debased coin usage by qualitatively and quantitatively analysing a large number of coins.^{10,15} The availability of micro-destructive elemental analysis has convinced museum curators to provide scientists with a good number and variety of coins. Spatial resolution has also minimised the impact of procedures aimed at removing corrosion layers which affect analysis. This is crucial for obtaining reliable results. Multi-elemental analytical information extracted from the untreated surface of a coin strongly reflects the composition of corroded layers and differs from that of an uncorroded matrix. When scientists became aware of this and adopted procedures to remove the corroded layer or to drill the coin so as to analyse the areas beneath any corroded layers, the ability of the roman coin-makers to enrich the surface of *denarii* with silver was discovered. Plating procedures were largely established from about 200 A.D. and spread to different

regions of the Empire.¹⁶ The silver enrichment of the coin surface alone meant that debasement continued, but without any change to the coins' outward appearance.

3.2 Anachronisms in painting compositions

Art fraud is a major problem facing museums, conservationists, conservation laboratories and dealers. A number of fakes are in fact housed in museums or private collections as certified works-of-art. Many artists have been successful as forgers, but few have been exposed as was the case for painting forgers Hans van Meegeren, David Stein or Elia Volpi. Skilful forgers have sometimes been able to carry out fakes so good as to place doubt in the minds of those authenticating them. For these reasons a variety of scientific methods have been looked to for the provision of support in discovering forgeries. Science became especially relevant when major museums began to submit their exhibits regularly for authentication. Its support became highly significant thanks to the non-destructive or micro-destructive analytical approaches made possible by spatially resolved methods. The high artistic and monetary value often attributed to potential fakes makes curators reluctant to allow invasive scientific investigations which may destroy parts of the object to a visible extent.

Multi-technique approaches and extensive analytical studies are often required to discover forgeries. However, X-ray fluorescence and emission methods have been shown to be a powerful aid as multi-elemental analytical information can highlight anachronisms in the composition of the work-of-art. The multi-elemental characterisation of pigments used in paintings may lead to the re-assignment of masterpieces when it is discovered that the pigments concerned were unavailable at the time the painting was initially supposed to have been carried out. The reconstruction of the history of pigments (Fig. 3 shows

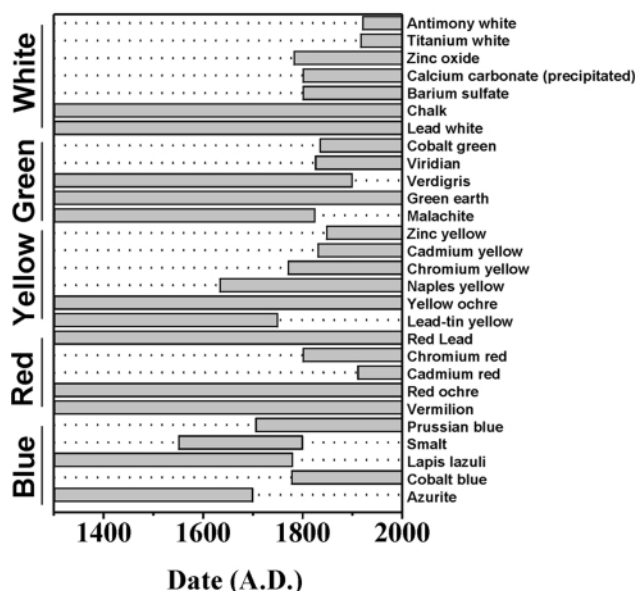


Fig. 3 Chronology of some of the most important pigments present in the traditional and modern palette (data from ref. 17). The chemical formulae of the pigments may be found in ref. 20.

the documented chronology of pigments present in the traditional and modern palette) may be gleaned from documentary sources as well as from the direct analysis of palettes used in studio studies. It is thus possible to obtain enough information to declare the re-assignments of paintings where the palette shows anachronisms.¹⁷ *Icescape*, attributed to Albert Cuyp (1620–1691), a Dutch Lowlands master, had to be reassigned once potassium and iron-containing blue Prussian Blue pigment

($\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$) in its sky-colouring was discovered. Prussian Blue was accidentally created by a German chemist, Diesbach, in 1704. The *St. Sebastian* attributed to the Italian painter Perugino (1446–1524) had a similar fate. It was seen to contain the cobalt and aluminium-containing blue pigment Cobalt Blue ($\text{CoO Al}_2\text{O}_3$) which was produced by the German chemists Gahn and Wenzel in 1777. Cobalt itself was only isolated in 1735. The beautiful *A Spring Landscape near Arles* given to be a Vincent van Gogh autographed original (1853–1890) was declared a fake on the basis of the presence of titanium in its white areas.¹⁸ With the support of other analytical techniques this was identified as titanium dioxide in the form of rutile. Titanium dioxide-based white pigments have only been available since the 1920s.

Palette anachronisms could appear as trivial faults for experienced forgers. However, it should be highlighted that changes in pigment preparation often lead to changes in impurity content. Zinc, for instance, not present in early Lead White pigment ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$), exceeds 1% in concentration from about 1870 because from that time ZnO rivalled its lead-containing counterpart on cost grounds. It was thus commonly used to adulterate the more expensive Lead White.

3.3 The Vinland Map

The conclusions drawn from the scientific examination of works-of-art have often sparked debates between scientists and art critics. The authentication of the *Vinland Map* was an exception to this. A debate over the conclusions drawn on the basis of various spatially resolved X-ray fluorescence and emission techniques sprang up between scientists themselves.¹⁹ The *Vinland Map* (Fig. 4) is a world map drawn on vellum showing a large island west of Greenland called Vinlandia Insula. The map is now owned by Yale University. It found its way to the United States in 1957, when a New Haven rare-book dealer bought it from an Italian book seller, and was dated as being from about 1440. This dating seemed to indicate that Leif Ericson's visit to the New World preceded that of Columbus. Moreover, the discovery of wormholes exactly matching those found in two medieval documents—the *Tartar Relation* and the *Speculum Historiale*—led to the supposition that the map had been bound between these two dated documents. This discovery was claimed as the most important cartographic discovery of the century. It was only after the study carried out by Walter C. McCrone that the map began to be suspected as a forgery. McCrone studied 29 tiny samples of the map by means of two spatially resolved X-ray emission techniques [SEM/EDX and electron microprobe analyser (EMA)] combined with diffractometric and microscopic techniques. His conclusions were essentially based on the presence of titanium dioxide in the form of anatase which corresponded to the yellowish areas apparently generated by the diffusion of the black ink on the parchment. Anatase was not available before the 1920s and microscope examination suggested that the yellowish iron-impurity-containing anatase had been used to simulate the capillary diffusion of the black ink. The black line thus appeared to be drawn onto the yellow line. McCrone's conclusions were discussed by a research group from the University of California who used a 4.5 MeV external beam line to analyse a large number of points of the *Vinland Map in situ* by means of PIXE. The beam used was collimated to 1×0.5 mm to match the width of the ink lines. The research group disputed the presence of titanium in the yellow areas whilst declaring much lower titanium percentages corresponding to only two-thirds of the ink areas overall. The highest level of titanium they encountered was 0.0062% by weight (corresponding to 10 ng cm^{-2} , typical uncertainty ± 0.2 , 3σ minimum detection limit 0.3) in comparison to the 28–35% found by McCrone in areas showing both yellow and black

colour. Titanium levels of this kind have often been found in ancient inks. Moreover, anatase could have been produced naturally during the production of medieval iron-based inks. Authenticity thus seems to be partially restored but further studies still need to be carried out for a definitive and unquestionable solution.

4 Spatially resolving photons: from ultraviolet to infrared

Light striking on a sample can be absorbed, scattered and transmitted. The study of the light absorbed provides information about the quantised energy levels of the sample molecules. In particular, the study of the radiation absorbed from the ultraviolet (UV) to the infrared (IR) (wave length ranging from 10 nm to 1000 μm) tells us about the energy of the electronic levels of the material under study and the energy associated to the molecular vibrations allowed for. The analytical potential of such study lies in the fact that the spectrum of the absorbed components often fingerprints the absorbing molecule. The study of the scattered component is also of analytical interest. In fact, even though the greater portion of the scattered component has the same frequency as the incident radiation (elastic or Rayleigh scattering) and only one in a million incident photons shifts in frequency (inelastic or Raman scattering), the availability of lasers for use as incident light sources has made it possible to use Raman scattering for analytical purposes. The positions in the spectrum of the bands due to the Raman scattered radiation is dependent on the molecular vibration of the scattering molecule. It should be noted that information on molecular vibration in Raman scattering complements that obtained in absorption studies.

4.1 UV, visible and IR spectroscopic methods

The first applications of UV, visible (VIS) and IR spectroscopic methods to studies of works-of-art go back to the 1930s.¹⁰ The first applications of these spectroscopic methods did not, however, deal with spatial resolution. The development of spectrophotometers which detect the diffuse-reflected radiation and mathematically Fourier transform the signal has led to

improvements in both sensitivity and spatial resolution.²¹ It should in any case be acknowledged that *image spectroscopic* methods were developed as early as the 1930s at the National Gallery in London. A visual colorimeter was used to acquire 2D-images from paintings illuminated with radiation at different wavelengths. Such methods, today greatly improved due to the use of CCD camera detectors, make it possible to identify areas of the painting emitting radiation at different wavelengths. From a certain point of view this implies that we are dealing with a spectroscopic method since specific compounds provide specific radiation when properly irradiated. FT-IR spectroscopy remains, however, the best way to obtain the widest variety of analytical information in the IR range. For this reason it is commonly used today in the undestructive study of works-of-art. FT-IR microscopy complements Raman spectroscopy (*vide infra*) in the characterisation of both the inorganic and organic constituents of archaeological and artistic objects. Both techniques require the sample to be placed under the objective of an optical microscope, the region to be analysed being focused with a spatial resolution in the range of a few tenths of microns. The best achievable spatial resolution is dependent on the wavelength of the incident radiation. The limitations of FT-IR microscopy when used in *in situ* studies of works-of-art mainly stem from the difficulty in providing fingerprints of specific compounds when heterogeneous matrices such as that of *tempera* paintings are under study. Another shortcoming lies in the interference caused by intense signals due to water and carbon dioxide present in the atmosphere.

The potential of *in situ* characterisation of works-of-art by means of instruments detecting radiation in the UV–VIS–IR ranges has increased since the availability of fibre optics. In the 1970s the first spectrophotometers using fibre optics to drive radiation onto the point to be analysed were set up at the National Gallery and the Courtauld Institute in London. Since then, fibre optic reflectance spectroscopy (FORS) has been used extensively in the study of ancient paintings.¹⁰ The potential of IR spectroscopy increased with the availability of FT-IR spectrometers. Initially, the major strength of such spectrometers lay in the small amount of material required to achieve good spectra. Fragments of an area equivalent to a few tenths of a μm^2 were sufficient (conventional IR spectrometers require sample areas in the range of a few mm^2), but only transmission measurements were possible with the energy throughput available. Successive improvements provided reflectance spec-

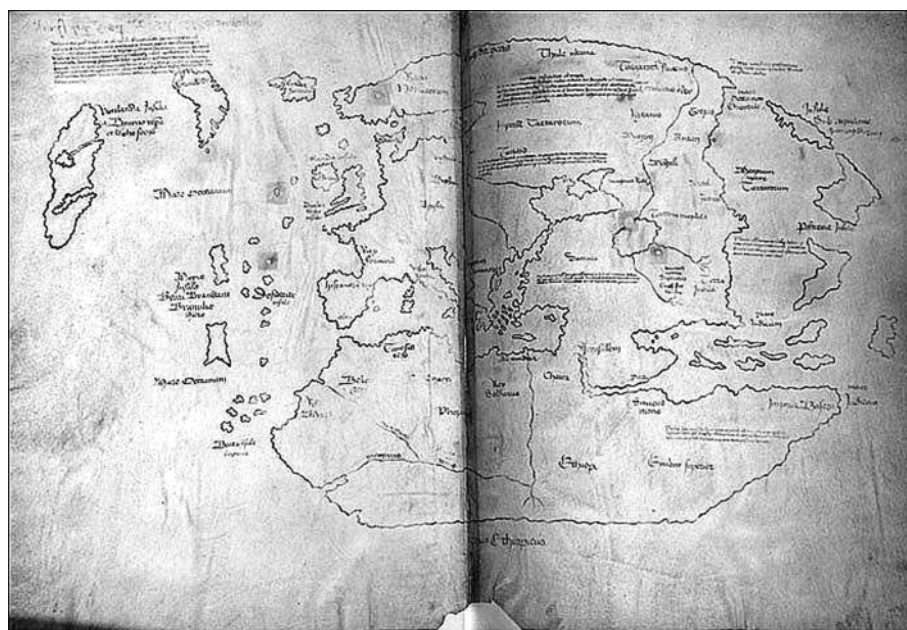


Fig. 4 The Vinland Map. (Source: Beinecke Rare Book and Manuscript Library, Yale University.)

tra and maps of selected areas which could then be recorded with a spatial resolution in the order of 20 μm .²¹

4.1.1 Amber provenance. “It will, of course, for ever remain a secret to us whether this amber is derived from the coast of the Baltic or from Italy, where it is found in several places, but particularly on the east coast of Sicily”. With this sentence of his book “Mycenae: a narrative of researches and discoveries at Mycenae and Tiryns” the German archaeologist Heinrich Schliemann (1822–1890), discoverer of the ruins of Troy and Mycenae, seemed to be challenging scientists to solve the puzzling question of the provenance of amber. Amber is a fossil resin, derived from coniferous trees. It comprises a complex mixture of molecules based primarily on monoterpenoid and diterpenoid structures. It has been used for ornamental purposes since prehistoric times when it was believed that amber was sunlight solidified by the sea waves. Understanding the provenance of amber made it possible to establish the earliest known trade routes which involved its transportation from northern to southern Europe around 5000 B.C. In the 1960s, IR spectroscopy contributed greatly to this discovery by providing evidence of differences in composition between Baltic amber and Sicilian amber. Transmittance IR spectra acquired from hundreds of amber samples made it clear that the vast majority of amber from prehistoric Europe derives from material originating in the Baltic coastal region.²² Differences in the absorption patterns generated by the vibrational stretching of C–O bonds (1110–1250 cm^{-1}) provided the analytical evidence of Baltic or non-Baltic provenance.

4.1.2 Ancient food. FT-IR spectroscopy is today commonly used in art conservation in order to identify pigments and organic media used in paintings in an undestructive manner as well as to identify and to map resins used for furniture finishes.¹⁰ Archaeology, however, has benefited most from the use of this technique to obtain chemical evidence of ancient food and beverages^{23,24}.

Food is fundamental for all human society, not only for nutrition and health but also in economic, social, and ritual life. Information about prepared food is therefore critical for an understanding of ancient cultures, but unfortunately examining the food of the past is extremely difficult. Food is normally consumed and leftovers usually decay. These problems are of particular relevance when residues of ancient beverages are to be studied. Fermented beverages are made from a variety of sugar-containing materials. Barley (*Hordeum vulgare* L.) was probably the first to be domesticated and used to make beer. This beverage first appeared in Mesopotamia around 6000 B.C.⁵ Wine followed the first beer production.

A small fragment of a yellowish residue present in a Neolithic jar found in the Hajji Firuz Tepe village (North of Iran) and dated 5400–5000 B.C. was analysed by means of diffuse-reflectance FT-IR spectroscopy.²³ The spectra showed features attributed to calcium tartrate after comparison with ancient and modern reference samples. This result, confirmed by means of chromatographic and UV spectroscopic methods, was the earliest chemical evidence for wine since tartaric acid occurs naturally in significant amounts (about 1%) only in grapes (*Vitis vinifera* L.). The calcareous environment of the site had converted the acid into calcium tartrate. Moreover, the shape of the jar confirmed its use as a liquid holder. A detailed study of the spectra (with peaks centred at 2926 and 2858 cm^{-1}) and their comparison with reference samples, together with the analytical evidence obtained from chromatographic and UV spectroscopic investigations, also confirmed the presence of an oleoresin extracted from the *Pistacia atlantica* Desf. terebinth tree. Alcohol-soluble resin was used to inhibit bacterial growth and improve the wine in taste and odour.

A similar analytical approach also led to the identification of the ancient organic material present in vessels found at Gordion

(Turkey) in a tomb dated at about 700 B.C.²⁴ The tomb is assumed to be that of the Phrygian King Midas. The study of the region at 1420, 1390, 1170 and 1120 cm^{-1} in the diffuse-reflectance FT-IR spectra of the methanol extracts of 14 food samples indicated that a mutton or goatmeat-based dish had been left in the vessels. The contemporary presence of bands due to long-chain esters of beeswax, calcium oxalate and calcium tartrate in the diffuse-reflectance FT-IR spectra of the methanol extracts of 16 beverage samples provided evidence of a mixed fermented beverage of grape wine (calcium tartrate), barley beer (calcium oxalate, also called “beerstone”), and honey mead (beeswax).

This study, which revealed one of the most comprehensive Iron Age drinking sets ever found, suggested that such food and drink was eaten at a feast before the interment of the King, thus providing fundamental chemical evidence for ancient cuisine in the Mediterranean area.

4.2 Raman spectroscopy

The use of Raman spectroscopy is pretty recent.^{10,20} The discrepancy with respect to other methods based on the absorption or transmission of light may be attributed to comparatively recent technical developments which have made it possible to enhance the intensity of the emitted Raman signal and detect it. In particular, micro-Raman spectroscopy has been shown to be a powerful technique for the *in situ* identification of both inorganic and organic ancient pigments. Applications of this kind have generated a wealth of papers which have already been overviewed in this journal²⁰ and will not be further detailed here. Instead we will look at the development of pigment analysis by micro-Raman spectroscopy which has led to an even greater number of studies, all confirming the immense potential of this technique for the undestructive identification of pigments used to decorate ancient books and manuscripts¹⁰ as well as to identify binding media and varnishes in paintings.²⁵ Pigments used in ancient pottery, faience, glassware, wall and easel paintings have been also identified by means of micro-Raman spectroscopy. In such cases, the extraction of tiny fragments of samples is often required since pigments are usually embedded into a matrix which prevents their direct analysis. Sections of the sample sometimes allow the identification and analysis of the pigment layer(s).

The evolution of micro-Raman spectroscopy in pigment analysis has seen a leading laboratory in the field at the University College of London establish an ancient pigments Raman spectra library available on the WEB.²⁶

Despite its potential in pigment identification, Raman spectroscopy has also been used for the investigation a variety of ancient materials.¹⁰ In fact, numerous ancient organic materials have been studied using laser exciting radiation in the near-IR region (mostly with an Nd-YAG laser emitting radiation at 1064 nm) to reduce the fluorescence that such kinds of materials often generate. Moreover, the special configuration of the spectrometer and the Fourier transformation of the signal (FT-Raman spectroscopy) have been shown to be of great relevance for studies concerning ancient organic materials. The differences in FT-Raman signals generated by amide groups can be found by comparing Raman spectra obtained from ancient mummy skin and fresh skin. Changes can also be seen in the Raman spectra of ancient natural fibres such as linen. This is due to the degradation suffered by the cellulose present in them.

The ability of Raman spectroscopy to indicate the presence of specific organic compounds can also be an aid in the detection of forgeries. The study of Raman bands due to collagen and hydroxyapatite provides a useful indication of the authenticity of ivory artefacts. By studying such signals it is also possible to

distinguish between ivory coming from Asian elephants, African elephants and extinct mammoths.²⁷

5 Spatially resolving particles: electrons and ions

Charged particles, such as electrons or ions, are easily focused by means of electrostatic or magnetic lenses. Analytical methods which collect electrons or ions thus fall quite easily into the spatially resolved methods field. Better performance in terms of spatial resolution is usually achieved by techniques that use electron or ion beams to stimulate the emission of a charged entity which holds the analytical information. Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) are two techniques of this kind. AES usually focuses and collects electrons. The electrons collected are Auger electrons. These electrons fall into an energy range which differs from the ranges of secondary electrons and backscattered electrons. They are emitted as a consequence of an internal rearrangement suffered by ionised atoms described by Pierre Auger in 1925. SIMS focuses ions and collects ions emitted as a consequence of the sputtering process. X-ray photoelectron spectroscopy (XPS) studies the electrons photoemitted from the core levels of atoms as a consequence of X-ray bombardment. XPS has low spatial resolution since it is difficult to focus the photoelectrons emitted from a small portion of the X-ray irradiated area. Modern XPS imaging equipment allows a 1–10 μm spatial resolution to be achieved, while modern AES and SIMS equipment usually work in the range of a few hundred Angstroms. Modern standard XPS equipment can achieve localised acquisitions within an area 300–500 μm in diameter.

Once the kinetic energy of photoemitted electrons and Auger electrons has been determined, reliable information concerning not only the emitting element but also the particular chemical state of the atom in question can be provided. The latter is particularly true for XPS. SIMS provides elemental and molecular information by mass analysing the ionic fragments sputtered from the sample.

A peculiar characteristic of the three above-mentioned techniques is that the information they provide refers only to the uppermost atomic monolayers of the sample (5–15 \AA beneath the surface of the material under study). Moreover, they challenge other analytical methods such as X-ray fluorescence and emission-based techniques in terms of range of detected elements. All elements may be virtually revealed by SIMS, while only H and He cannot be detected by XPS and AES.

The earliest applications of XPS to the study of archaeological artifacts date back to the beginning of the 1970s, while AES and SIMS began to be used at the beginning of the 1980s.¹⁰ So far these techniques have found a relatively limited number of applications. A wider range of ancient material has been studied by XPS. Ancient pottery, metallic objects, paintings and pigments have all been studied with the principal aim of making use of the chemical state identification potential of XPS. The degradation suffered by ancient paper documents and manuscripts and the efficacy of processes which compensate for acidification caused by ageing and paper manufacturing procedures have also been studied with this technique.¹⁰ A more limited range of ancient materials have been studied by AES. This is essentially due to the difficulties encountered when studying non-conductive material and to the compositional modification in a wide range of organic and inorganic based materials caused by the electron bombardment that AES requires. Metallic artifacts have been studied by means of this technique and mapping facilities have been used to image the distribution of corrosion products within the matrix of ancient artifacts.²⁸

SIMS has so far been used less commonly in the field of art and archaeological studies. Ancient ceramic material²⁹ has been

studied by SIMS while the mapping potential of this technique has also been applied in the study of ancient bronze artefacts³⁰ (Fig. 5).

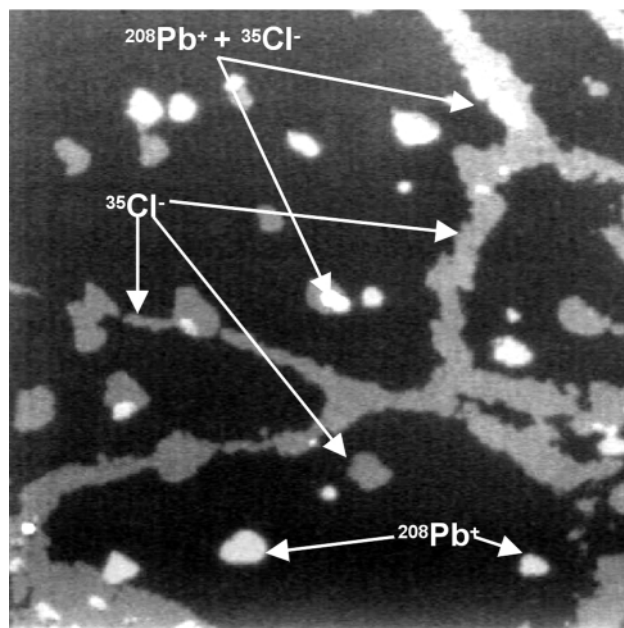


Fig. 5 Secondary ion map showing the distribution of $^{208}\text{Pb}^+$ and $^{35}\text{Cl}^-$ in a section of the bronze matrix of an Early Iron Age body-filled bracelet (*armilla*). The imaged area is $75 \times 75 \mu\text{m}$. Three different gray levels are used to distinguish between regions constituted by $^{208}\text{Pb}^+$ or $^{35}\text{Cl}^-$ alone, or by combined $^{208}\text{Pb}^+$ and $^{35}\text{Cl}^-$.

Ions are also analysed with spatial resolution by the mass spectrometric technique called laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). This technique sorts by mass and detects ions that are generated when material, ablated from the surface of a solid object by means of a suitable laser probe, is introduced to a high temperature plasma which dissociates molecules and ionizes atoms. It allows the coupling of the spatial resolution determined by the laser probe diameter in the range of very few tenths of microns with a detection limit in the range of ppm–ppb, and since the 1980s has found applications in the qualitative and quantitative elemental characterisation of a range of solid materials including metals, shells, teeth, bone and stone.¹⁰ Potential for LA-ICP-MS trace elemental analysis has recently found application in fingerprinting ancient Egyptian basalt quarries³¹ and in profiling elements in weathered marbles.³² It is expected that the availability of further fundamental studies concerning LA-ICP-MS will allow this spatially resolved technique to be proposed as one of the most important in the field of quantitative trace elemental analysis of artistic and archaeological materials.

The spatial resolution of electrons has also led to the development of transmission electron microscopy (TEM) and scanning electron microscopy (SEM).¹⁰ In TEM an electron beam accelerated by a power source, usually in the range of 100–400 kV, is focused onto the sample. A magnified image is obtained on a fluorescent screen by focusing the transmitted electrons with a system of electromagnetic lenses. Transmitted electrons also undergo scattering processes (electron diffraction) which contribute to the contrast of the image and also provide analytical information. In SEM a primary electron beam (20–40 kV) is used to generate an image that is obtained by collecting secondary or backscattered electrons. The image reflects the morphology of the scanned surface and carries only limited and not explicit analytical information. The great advantage of TEM as opposed to SEM or optical microscopy lies in its higher resolving power. Resolution in the order of 3–5 \AA can be obtained thanks to the small wavelength associated with accelerated electrons (e.g., an electron beam

accelerated by 100 kV is associated with a wavelength of 0.037 Å). It should be pointed out, however, that transmitting an appreciable fraction of the incident electron beam requires the sample to be prepared in the form of a very thin foil no thicker than 2000 Å. The impact of TEM analysis on tiny fragments of samples to be studied is thus definitely destructive. SEM allows fragments of samples or small objects to be imaged. A thin conducting evaporated coating is often deposited on to the surface of non-conducting samples to avoid unwanted charging effects. EDS detectors are often mounted in both TEM and SEM to allow elemental analyses of specific regions of the sample. In this way elemental information can be coupled with morphological information. TEM also provides diffractometric information which may be gleaned from the scattering of the electrons.

SEM is in daily worldwide use in conservation laboratories: for overviews of SEM applications to the study of works-of-art and archaeological remains see refs. 10 and 33. Special emphasis on SEM applications is not appropriate in this review due to the very limited analytical information that SEM provides.

The use of TEM in the fields of art and archaeology is relatively recent and a limited number of applications have been found so far. One of the earliest uses of this technique clarified the reasons for the dichroic effect displayed by the Lycurgus Cup.³⁴ The cup, which is a superb example of ancient Roman skill in glass-making, illustrates the myth of King Lycurgus who was strangled by Ambrosia transformed into a vine by Diana. The glass of the Lycurgus Cup appears to be of a deep wine-red in transmitted light while it is pea-green in reflected light. This dichroism was attributed to the presence of rounded and polygonal particles 50–100 nm in diameter and 10 µm on average apart in the glass. The particles are made up of silver (66.2 %at.), gold (31.2 %at.) and copper (2.6 %at.).

5.1 Dating manuscript inks

Detection of fraud also involves documents and manuscripts. Spatially resolved analytical techniques have been used to provide information which points to the authenticity of ancient documents. Auger electron mapping has been proved to be of particular relevance in dating ancient manuscripts on paper. This method enables us to date the time elapsed since the ink was drawn on the paper.

The basic feature of this application of scanning auger microscopy (SAM) for the dating of manuscript inks is the time-dependent migration of metal ions from the ink.³⁵ This migration causes the formation of a skewed tail on the ink edge profile beyond the dried capillary drawn ink area which increases with time. Ion migration is assumed to be related to the presence of carboxy groups in the cellulose based fibres upon which the ink is deposited. It develops following a form of ion exchange with the concentration gradient.

The high lateral resolution of SAM (up to a few hundred Å) makes it possible to emphasize the distribution of a selected element along the ink profile simply by performing line scan acquisition. Iron is the most common element used for SAM dating purposes owing to the wide use of ferrogallic inks in the past. A typical profile, if possible taken from fibrils running perpendicular to the ink line so as to avoid morphological induced alterations of the elemental profile, shows two shoulders at either side of the curve which defines the area on which the ink was distributed by the nib of the pen (Fig. 6). These shoulders are generated by diffusion driven by capillary forces at the surface of the fibre. The area under the tail that shows up beyond the capillary diffusion induced shoulder is used for calculating the period of time that has elapsed since the ink was deposited on the fibre. With methods of this kind

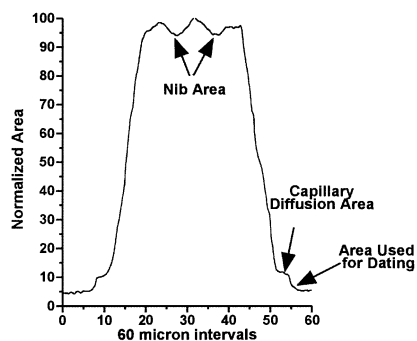


Fig. 6 Auger lateral scan showing the distribution of iron across the ink profile. The shoulders at either side of the curve are generated by diffusion driven by capillary forces at the surface of the fibre. The area under the tail that shows up beyond the capillary diffusion induced shoulder is used for calculating the period of time that has elapsed since the ink was deposited on the fibre. Reproduced with permission from R.J. McNeil, in *Archaeological Chemistry III*, ed. J. B. Lambert, Advances in Chemistry Series 205, p. 255. Copyright 1984 American Chemical Society.

documents dated for the period 1350–1950 have been dated with an accuracy of around ± 22 years.³⁵

5.2 Antique music wire

The restoration of the original sound of ancient harpsichords and other wire-strung musical instruments requires the selection of appropriate wire for each string. Ancient documents lack complete information for string material. The study of remnants of the original material is therefore the only reliable way to reproduce original performance. Between the end of the 1500s and the beginning of the 1600s a modification was introduced in the making of wire-strung instruments: they were made longer. This change, which was a demonstration of the availability of stronger wire to produce the same frequency with a longer string, can be attributed to the introduction of steel wire. In fact, it was at the beginning of 1600s that blister steel was first produced by introducing carbon into wrought iron with a process known as cementation. However, quantitative SIMS analysis of fragments of ancient wire samples dated at 1732 (Vater, 0.33 mm in diameter), 1733 (Blancher, 0.23 mm in diameter) and 1782 (Shudi, 0.29 mm in diameter) showed unexpected results.³⁶ Phosphorus content in the range of 0.1–0.2% wt. was found to couple a quite low carbon content (<0.007% wt.). The wires were not steel and contained an alloying element that was known to make steel brittle when cold-worked. The surprise of this result can be inferred by considering that the presence of phosphorus in iron was discovered only in 1784 and that today's common techniques of strengthening iron containing a small amount of carbon with phosphorus is documented only from the 1800s. It was a casual discovery, possibly made in Nuremberg in 1601, that led to a change in the proportions of wire-strung musical instruments. Iron which had been cleaned of inclusions by means of a special fining method and which did not contain sulfur (often associated with phosphorus but, in contrast to the latter, easily detectable by its odour) made stronger wire. The casual combination of such processes ensured the highest content of phosphorus to be present in a low-carbon-containing iron, thus enabling longer wire to be produced.

5.3 Maya blue paint

The early people in Mesoamerica and colonial Mexico used to decorate pottery and painted pictures on walls with a blue pigment found nowhere else in the world. The unusual properties of this pigment, called *Maya Blue*, have ensured the

preservation of the beautiful paintings of ancient Mesoamerican populations such as the Maya and Aztec peoples but have also prompted us to understand its puzzling nature. Maya Blue is stunningly stable and resistant to diluted mineral acids, alkali and solvents. It is resistant to moderate heat (temperatures up to 250–300 °C) as well as to oxidant and reducing agents. It is also not significantly affected by biological corrosion. Such properties, which have ensured the brightness of the pigment throughout the centuries, have been clarified in part thanks to TEM studies.³⁷

The Maya Blue pigment was known to contain clay and indigo dye. The clay was mainly constituted by palygorskite, probably corresponding to the material that the Mayas called *Sacalum*. The indigo dye, called *añil*, was probably extracted from a plant called *Xiuquilit*. This dye, however, is not resistant to acid and biological agents and thus does not account for the colour of Maya Blue. TEM imaging revealed the presence of two different mixed regions in the microscopic structure of Maya Blue: a region with well shaped crystals and a region with small particles with an average dimension of 4 nm, embedded in amorphous SiO₂. The crystals were identified as palygorskite but showed a lattice period (~14 Å) three times the value observed in standard palygorskite samples along the {400} direction. This was attributed to the intercalation of the indigo molecules in the palygorskite structure. The superstructure partially accounts for the stability of the pigment. The small particles, mainly composed of Fe and Cr in both metallic and oxidised form, also contribute to the exceptional properties of the Maya Blue. They scatter the light and partially contribute to the blue colour of the pigment as a consequence of both the linear and non-linear optical properties of these nanoparticles. Their oxidised nature and their encapsulation in the amorphous SiO₂ explain the high stability of the Maya Blue.

TEM imaging thus revealed the complex nanostructured nature of Maya Blue which has preserved the beauty of ancient Maya paintings.

6 Concluding remarks

The ability to spatially resolve analytical information has been a significant breakthrough in the study of remnants of our past. Non-invasive or micro-invasive analytical approaches have allowed access to a great variety of unique works-of-art, thus unravelling the history they are a part of. Steps in man's progressive ability to manipulate and modify matter have also been identified and ancient customs have been discovered.

The complex nature of the objects studied has often required the use of multi-technique analytical approaches and the application of the entire analytical potential of spatially resolved techniques. With techniques that need high energy, high power and high flux for the bombarding particles it is sometimes crucial to evaluate impact on the object's integrity. This is particularly true when *in situ* spatially resolved studies of organic material are going to be performed. Experimental conditions should be adequately evaluated and selected in such cases to minimise damage to the analysed works-of-art. X-ray fluorescence and emission methods, which are often used for *in situ* analysis of works-of-art, can suffer this drawback. Other techniques such as XPS, AES and SIMS, which operate under potentially harmful conditions for artistic and archaeological artefacts, do not allow the *in situ* analysis of material that does not fit chamber analysis in size and shape. Tiny fragments are usually analysed by means of these techniques. However, damage induced by the bombarding particles is also to be avoided because the chemical composition of the sample surface could differ from the original one as a consequence. Techniques such as FT-IR microspectroscopy, micro-Raman spectroscopy, and FORS come pretty close to the ideal. They

allow the study of objects that can be fitted under probes and transfer low-powered radiation onto the analysed area.

It is expected that future applications will further demonstrate the analytical potential offered by spatially resolved techniques in the field discussed and that even more integrated non-invasive multi-technique procedures will become available for the study of both the organic and inorganic constituents of ancient materials.

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