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ORIGINAL PAPER

# Pigments, dyes and inks: their analysis on manuscripts, scrolls and papyri

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## Abstract

This chapter provides an overview of some of the materials used to write and decorate different types of manuscripts, i.e. inks, pigments and dyes, and of the different scientific methods and techniques available for their analysis and characterisation. The target audience is not only made of scientists but also curators, conservators, students and practitioners who want to know more about the technical examination of manuscripts and wish to appreciate the context of the scientific analysis of this type of objects. The possible types of approach to the scientific investigation of manuscripts are discussed, and the most frequently used analytical techniques are grouped according to their level of invasiveness and destructiveness. The chapter also contains a quick guide to some of the main questions that may arise about manuscripts, and explains how scientists can help to address them. Finally, a general protocol for the scientific analysis of manuscripts is illustrated.

**Keywords** Manuscripts · Papyri · Scrolls · Pigments · Dyes · Inks · Scientific analysis

## Premise

This Topical Collection (TC) covers several topics in the field of study, in which ancient architecture, art history, archaeology and material analyses intersect. The chosen perspective is that of a multidisciplinary scenario, capable of combining, integrating and solving the research issues raised by the study of mortars, plasters and pigments (Gliozzo et al. 2021).

The first group of contributions explains how mortars have been made and used through the ages (Arizzi and Cultrone 2021, Ergenç et al. 2021, Lancaster 2021, Vitti 2021). An insight into their production, transport and on-site organisation is further provided by DeLaine (2021). Furthermore, several issues concerning the degradation and conservation of mortars and plasters are addressed from practical and technical standpoints (La Russa and Ruffolo 2021, Caroselli et al. 2021).

The second group of contributions is focused on pigments, starting from a philological essay on terminology (Becker 2021). Three archaeological reviews on prehistoric (Domingo Sanz and Chieli 2021), Roman (Salvadori and Sbrolli 2021) and Medieval (Murat 2021) wall paintings clarify the archaeological and historical/cultural framework. A series of archaeometric reviews illustrate the state of the art of the studies carried out on Fe-based red, yellow and brown ochres (Mastrotheodoros et al. 2021), Cu-based greens and blues (Švarcová et al. 2021), As-based yellows and reds (Gliozzo and Burgio 2021), Pb-based whites, reds, yellows and oranges (Gliozzo and Ionescu 2021), Hg-based red and white (Gliozzo 2021) and organic pigments (Aceto 2021). An overview of the use of inks, pigments and dyes in manuscripts, their scientific examination and analysis protocol (this paper) as well as an overview of glass-based pigments (Cavallo and Riccardi 2021) are also presented. Furthermore, two papers on cosmetic (Pérez-Arantegui 2021) and bioactive (antibacterial) pigments (Knapp et al. 2021) provide insights into the variety and different uses of these materials.

This article is part of the Topical Collection on *Mortars, plasters and pigments: Research questions and answers*

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## Introduction

It is perfectly reasonable to think that manuscripts, or more generally works on pith, papyrus, paper or parchment, are fragile and easily damaged. And yet many have survived for centuries and even millennia, giving us testimony of peoples and ages long past. Scrolls, concertina manuscripts and bound volumes, both in their content and materiality, continue to represent a unique source of information about our history.

This chapter will provide an overview about some of the materials used to write and decorate these objects, i.e. inks, pigments and dyes, and about the different scientific methods and techniques available for their analysis and characterisation. Where possible, I will be citing publications and reference material that are easily retrievable (in public libraries or the web).

I will use the word 'manuscript' in its etymological meaning ('written by hand'), encompassing various types of objects that serve a similar function, i.e. recording and preserving information in writing on a flexible, transportable substrate—including scrolls, codices, etc.

## Manuscripts: a timeline

When was the first manuscript made and what did it look like? The earliest unearthed so far are papyri scrolls from the fourth dynasty in ancient Egypt, some 4600 years ago.[1, 2] Elsewhere, other civilisations were writing on different types of substrates, made by processing other plant-based materials, hemp, linen and cotton rags, and animal skins. Parchment, although it was not known with this name yet, was in use in Asia Minor in the fifth century BCE and was widely used in the western world for centuries. According to Szirmai (1999), the appearance of the codex can be traced back to the early centuries of our era, while according to Roberts and Skeat (1983), the earliest bound books originated from the Roman empire; their pages were usually made of papyrus, parchment or paper. An enduring concept, bound books have resisted well the test of time and are still a staple for the recording and dissemination of knowledge to this day.

[1] https://www.smithsonianmag.com/history/ancient-egypt-shipping-mining-farming-economy-pyramids-180956619/. Accessed 7 December 2020.

[2] Please note that the earliest example of a papyrus roll is said to be the blank roll from the tomb of Hemaka at Saqqara, dating from the beginning of the third millennium BC, as reported on page 227 in Leach and Tait (2000).

## Analysis approach: to damage or not to damage?

Over the past two decades, researchers have used many analytical techniques in order to characterise inks, pigments and dyes, and obtain from them additional information about each object as a whole, its societal, financial, technological and historical context (Manca et al. 2019).

It is helpful to divide them into groups depending on the type of information that they can provide: elemental information (what elements from the periodic table—such as copper, iron, lead, gold—are present?), molecular information (how are the elements arranged and what specific molecules are present?) and physical information (such as colour). A synopsis of the main scientific techniques, grouped according to the type of information they can provide, is shown in Table 1.

In the past, only a restricted number of scientific methods was available, which not only provided relatively limited results but often relied on significant destructive sampling (Flieder 1968). Fortunately, non-invasive, non-destructive techniques are now commonplace (Clark 2005; Miliani et al. 2010; Burgio 2011; Analytical Methods Committee 2015; Christiansen et al. 2017; Grazia et al. 2018)

**Table 1** Synopsis of a selection of scientific analysis techniques, grouped by the type of information they provide

| | Name |
|---|---|
| Elemental | Energy-dispersive X-ray analysis (EDX) |
| | Laser-induced breakdown spectroscopy (LIBS) |
| | Particle-induced X-ray spectroscopy (PIXE) |
| | X-ray fluorescence spectroscopy (XRF) |
| Molecular | Attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) |
| | Chromatography |
| | Fibre-optic reflectance spectroscopy (FORS) |
| | Fourier-transform infrared spectroscopy (FTIR) |
| | Hyperspectral imaging (HIS) |
| | Multispectral imaging (MSI) |
| | Raman spectroscopy |
| | Spectrofluorimetry |
| | Surface-enhanced Raman spectroscopy (SERS) |
| | Ultraviolet, visible, near-infrared spectroscopy (UV–vis-NIR) |
| | X-ray diffraction (XRD)* |
| Physical | Computed and micro-computed tomography (CT and μCT) |
| | Microfade testing |
| | Scanning electron microscopy (SEM) |
| | X-radiography |

Commonly used acronyms are provided where available

*Strictly speaking, X-ray diffraction should not be characterised as a molecular technique, but this simplification is adopted here for ease of reference

and they should be used preferentially before resorting to methods that involve sampling or in situ destructive interventions.

A clarification is needed here: there are methods that do not involve sampling, but are nonetheless invasive and/or destructive. All analytical techniques are effectively on a spectrum from totally non-invasive and non-destructive (preferable) to destructive and invasive on some scale. This will be discussed more in detail below. A simplified glossary is provided in Table 2 for ease of consultation.

Occasionally, there are times where samples are already available because they have naturally detached from the object due to damage or ageing (this is often referred to as 'self-sampling'). It is not uncommon to find pigment debris (both as dust and/or fragments) nested in the gutters between the pages of a manuscript or codex (Chaplin et al. 2005). Although it is not always possible to reconstruct where exactly on a page they have come from, these fragments do provide the opportunity for types of analysis that would not otherwise be considered because they are too intrusive. In other cases, a deliberate choice is made to remove and sacrifice a small sample in order to obtain valuable information from it, which would otherwise be inaccessible (Melo et al. 2019).

A separate argument can be made about in situ minimally invasive techniques, i.e. methods that do not require sampling, but nonetheless alter or damage the object under observation. Typical examples include surface-enhanced Raman spectroscopy (SERS, see Analytical Methods Committee 2017), laser-induced breakdown spectroscopy (LIBS, see Analytical Methods Committee 2019), attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR, see Nodari and Ricciardi 2019) and microfading (Ford 2018; Pretzel 2021). Circumstances may justify adopting such techniques, depending on how crucial the questions being asked are, what the condition of the object is and how small the area affected is. An object may lend itself to minimal sampling because of its already poor condition. The choice of technique must always be weighed against the value of the information that might be gained by the analysis. It is good practice to document carefully any sampling; this may include macro- and micro-photographs to record the area being sampled or examined using minimally invasive techniques, before and after the analysis.

The past two decades have also seen the development of new portable equipment, which makes it possible for the analysis to take place without transporting the manuscript to a laboratory, thereby reducing the chances of damage to the object. In the early days, the performance of portable pieces of kit was not as efficient as that of bench-top equipment, which usually afforded better sensitivity and spectral and spatial resolution; however, the newest generations of portable equipment show greater promise, and provide good quality results (Bersani et al. 2016; Brunetti et al. 2016; Nicholson et al. 2016; Nodari and Ricciardi 2019; Ricciardi et al. 2019; Crippa et al. 2020; Senesi et al. 2020). It must be clearly stated that portable equipment are still not comparable to bench-top instrumentation and they are best used for preliminary investigations or when no better alternative is available.

It is worth remembering that technological advancements occur all the time, and allow for new possibilities. What is impossible to do today with the means at our disposal, without resorting to sampling or to destructive approaches, may become feasible tomorrow. New developments may reduce the size of the sample needed to carry out a specific type of investigation, or may allow us to perform the analysis non-destructively and in situ.

Table 3 shows the most common analytical techniques grouped according to their invasiveness and destructiveness. Selecting the most appropriate ones can be daunting, and always depends on the specific research and conservation questions on the table. This in turn will determine the level of invasiveness/destructiveness chosen in each case.

## Inks, pigments and dyes

There are many schools of thought about the terminology to use when describing and discussing artists' materials, and often confusion ensues when addressing a diverse,

**Table 2** Simplified glossary of terms pertaining to the type of analytical technique and analysis approach

| Definition | Explanation |
|---|---|
| In situ | (Latin) On the object itself |
| Non-invasive | No sampling is required, and no contact between the object and the instrument is involved |
| Invasive | Sampling from or contact with the object is required |
| Minimally invasive | The consequences of sampling from and/or contact with the object are effectively invisible from a macroscopic perspective |
| Destructive | The area under analysis is destroyed or used up |
| Non-destructive | The area under observation remains intact and can be used for additional investigations |

**Table 3** Synopsis of the most commonly used analytical techniques for the analysis of inks, pigments and dyes, grouped by their invasiveness and destructiveness

| | Non-destructive | Micro-destructive |
|---|---|---|
| Non-invasive | Raman<br>FTIR<br>UV–vis-NIR and FORS<br>Spectrofluorimetry<br>XRF<br>PIXE<br>XRD*<br>MSI and HSI<br>CT and μCT<br>SEM* | |
| Minimally invasive | SERS*<br>ATR-FTIR* | LIBS<br>Microfading |
| Invasive | SEM (on samples) | Chromatography |

Asterisks mark where the techniques are meant to be used in situ in order to be classified as non-invasive or minimally invasive

multidisciplinary audience. In the common parlance, it is not unusual to see the word 'ink' being used to cover anything that can be used to decorate or write on a manuscript; 'pigment' and 'dye' are also often used indifferently and arbitrarily to indicate anything that can be used to paint or colour; more often, the word 'pigment' is used as a substitute of 'inorganic colouring material', while 'dye' is a stand-in for 'organic colouring material'.

While there are many official definitions,[3, 4] in this chapter I will assume the following (with caveats highlighted when necessary):

1. Ink—any relatively dark material used to write text
2. Pigment—essentially insoluble material, often but not exclusively inorganic in origin
3. Dye—essentially soluble material, often but not exclusively organic and of natural origin

In this section, I will briefly mention specific analytical techniques in the context of the material designations, but will also go into further details later on, within the sections that deal more specifically with typical questions asked concerning manuscripts.

## Inks

The earliest inks were made using easily obtainable materials, mostly carbon-based (Winter and West FitzHugh 2007): soot from lamps ('lamp black'), charcoal from charred wood and other vegetable matter, or graphitic materials found in nature.[5] Eventually, bone black and ivory black,[6, 7] obtained from the charring of bones and ivory, were also used, as was iron gall ink (iron gallotannate, traditionally obtained from oak galls and documented in vague terms by Pliny the Elder in the first century CE), the ink of choice in the West from the late Roman empire until the twentieth century.[8]

In the first instance, it would be tempting to identify these inks by eye: iron gall inks tend to have a more brownish hue than carbon-based blacks. But there are numerous exceptions to this and it is safer to rely on techniques that do not leave room for interpretation. Raman spectroscopy provides a relatively straightforward, non-destructive route to identification, and can record a distinctive fingerprint from both carbon-based materials and iron gall inks (Lee et al. 2006; Burgio et al. 2010; Edwards 2018).

Other non-destructive techniques include FTIR (Diaz Hidalgo et al. 2018), XRF and particle-induced X-ray emission (PIXE), which can suggest an identification based on the presence of minor components such as iron and other metals (Budnar et al. 2006; Aceto et al. 2008). Multispectral imaging can also help (Striova et al. 2014; Kogou et al. 2015; Manca et al. 2019)—carbon-based materials are still visible in infrared light, while iron gall inks become transparent and therefore disappear in the resulting image (see Fig. 1 and Burgio 2019). Combinations of analytical methods can also be used, e.g. macro-XRF and hyperspectral imaging (Pouyet et al. 2017; Corregidor et al. 2019; Tournié et al. 2019).

Carbon black has been found on examples of Egyptian papyri (Burgio and Clark 2000; Olsson et al. 2001), medieval manuscripts (Aceto et al. 2008; Burgio et al., 2010; Grazia et al. 2018), more recent manuscripts (Lee et al. 2008) and Japanese woodblock prints (Vermeulen et al. 2020). Iron gall inks were identified on manuscripts as early as the first part of the eighth century (Burgio et al. 2013), and on later manuscripts (Lee et al. 2006; Burgio et al. 2010), musical scores, handwritten compositions (Del Carmine et al. 1996, Hahn 2010; Manca et al. 2019), etc.

Researchers have recently hypothesised the possibility to date manuscripts through the analysis of the inks in them (Goler et al. 2019).

Sometimes mixtures were used, when carbon black was added to iron gall ink to improve its colour. Various types of carbon blacks were also used as black pigments in their own right, and in very few cases, iron gall ink was also identified

[3] https://colour-index.com/definitions-of-a-dye-and-a-pigment. Accessed 7 December 2020.

[4] https://www.winsornewton.com/row/articles/colours/spotlight-on-colourants-dyes-pigments/. Accessed 7 December 2020.

[5] http://cameo.mfa.org/wiki/Carbon_black. Accessed 7 December 2020.

[6] http://cameo.mfa.org/wiki/Bone_black. Accessed 7 December 2020.

[7] http://cameo.mfa.org/wiki/Ivory_black. Accessed 7 December 2020.

[8] http://cameo.mfa.org/wiki/Iron_gall_ink. Accessed 7 December 2020.

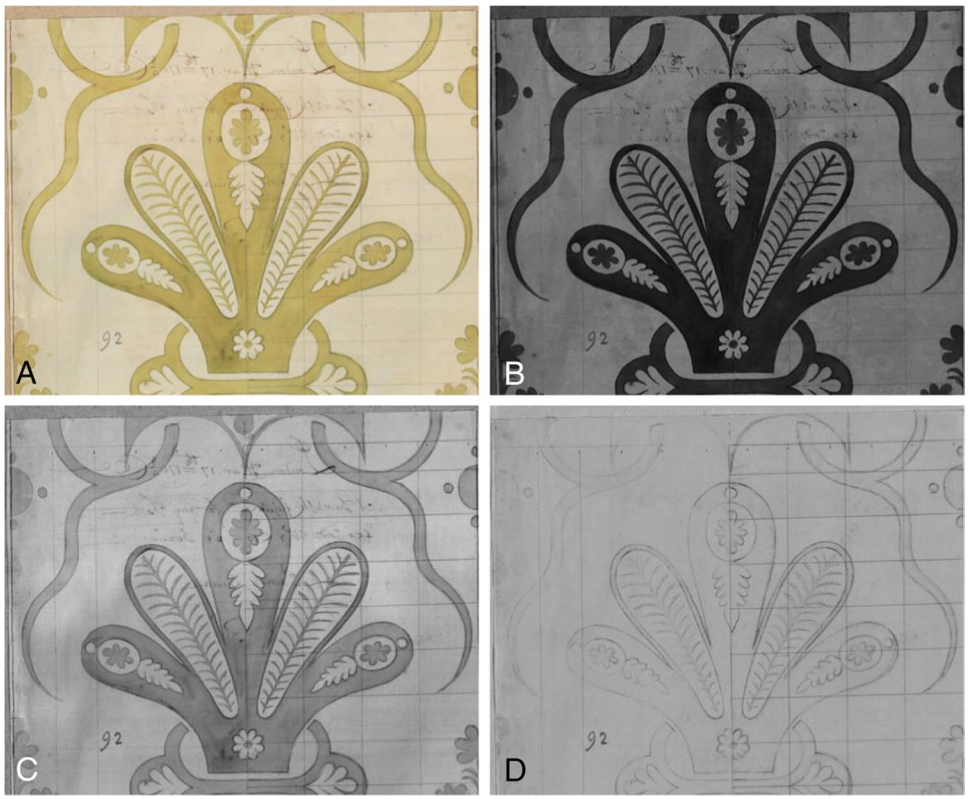


**Fig. 1** Leman design 21 (V&A accession number E.1861:21–1991) analysed by Vis–NIR multispectral imaging: colour image (**A**), and reflectograms centred at 415 nm (**B**), 630 nm (**C**) and 2550 nm (**D**). The handwriting at the top of the page, coming through from the verso (**A**), is traced with iron gall ink: it is still discernible in the reflectograms acquired in the visible spectra range (**B** and **C**), while it becomes invisible under infrared light (**D**). In contrast, the grid and the underdrawing are traced with a carbon-based material, and remain visible. Experiments made in the framework of Iperion-CH grant n. 654,028, see Manca et al. 2019 for the experimental details

in its use as a colouring pigment rather than a writing material (Burgio et al. 2010; Aceto and Calà 2017).

## Pigments

Many publications and resources have been dedicated to the use of pigments through the ages (Harley 1982; Feller 1986; Roy 1993; West FitzHugh 1997; Berrie 2007; Eastaugh et al. 2007; Douma 2008; Cameo Materials Database n.d.); therefore, this topic will be discussed only in general terms here.

Going back to the earliest surviving manuscripts, i.e. Egyptian papyri, the range of available pigments was limited, and mostly included a variety of naturally available materials such as iron-based earths and common minerals, but eventually synthetic materials such as Egyptian blue, Egyptian green and cobalt-based blues started to emerge (Di Stefano and Fuchs 2011; Scott 2016; Siddall 2018). The Egyptians had other artists' materials available, such as lapis lazuli and lead antimonate, but they were used for other decorative purposes and were not usually ground to a powder for application to papyri as painting materials.

Over the centuries, more and more materials became available, through discovery and exploitation of natural resources; observation of degradation processes that involved everyday objects (e.g. the corrosion of metallic lead and metallic copper when exposed to vinegar, and the consequent formation of lead white (Gettens et al. 1993a) and verdigris (Kühn 1993), respectively); chemical experimentation (synthetic vermilion, see Gettens et al. 1993b); cross-pollination from other artistic disciplines, for example, the use of ground by-products of the glass and ceramics industries, as discussed by Berrie and Matthew (2005), such as lead antimonate (Wainwright et al. 1986) and smalt (Mühlethaler and Thyssen 1993); introduction of materials used in other crafts, such as metallic bismuth (Burgio et al. 2009a; Trentelman and Turner 2009); as well as via sheer serendipitous discovery (e.g. Prussian blue, see Berrie 1997, and mauveine, see Cañamares et al. 2014).

The modern era saw an explosion of new synthetic materials, many of which were enthusiastically embraced by artists (Craddock 2009). Some of these vibrant pigments and dyes were used on contemporary manuscripts and paper-based objects (Cesaratto et al. 2017), although their presence on older manuscripts usually indicates a recently retouched object or an outright forgery (Burgio and Clark 2000; Durán et al. 2011).

## Dyes

The use of dyes throughout history has already been covered by several authors (Harley 1982; Feller 1986; Roy 1993; West FitzHugh 1997; Berrie 2007; Eastaugh et al. 2007; Douma 2008; Abel 2012; Cameo Materials Database n.d.), and will not be discussed in detail here.

Dyes were originally extracted from natural sources (plants, roots, insects, etc.), and their use is documented since antiquity (especially woad and indigo, kermes, lac, madder, Tyrian purple and orchil—see Lucas 1962; Cardon 2007; Melo 2009).

A sudden influx of modern synthetic dyes was seen in the second half of the nineteenth century, when William Henry Perkin, during his attempt to synthesise the antimalarial drug quinine, stumbled instead on what would soon after be known as mauveine: aniline dyes were born, and many other new classes of synthetic dyes would follow in the early twentieth century.

Until relatively recently, the analysis and characterisation of dyes on manuscripts were perceived as difficult, and all but impossible if a non-destructive approach was chosen. Only a very small number of dyes could be identified non-destructively and in situ: under UV light, madder usually exhibits a very distinctive fluorescence (Schweppe and Winter 1997), which can be used to infer the presence of this dye. Indigo easily gives a very recognisable Raman spectrum; it was first reported on textiles by Coupry et al. in 1997, but had been routinely identified on medieval manuscripts since at least 1996 (Burgio 2000). Berberine and gamboge also give a recognisable Raman spectrum (Burgio and Clark 2001).[9] However, most dyes of natural origin (but also the modern, synthetic 'Perkin dyes') are difficult to identify by Raman microscopy, unless its minimally invasive incarnation, surface-enhanced Raman spectroscopy (SERS), can be used (Melo et al. 2016; Manca et al. 2019). FORS and UV–Vis reflection and emission spectroscopy (Leona and Winter 2001; Miliani et al. 2010; Doherty et al. 2013; Aceto et al. 2014) can suggest what type of dye is present, but often doubts remain. And while SERS can help with the identification of manuscript dyes in situ, until recently it involved the direct contact of the painted surface with a small amount of wet reagents (Whitney et al. 2006; Pozzi et al. 2013; Castro et al. 2014; Melo et al. 2016; Analytical Methods Committee 2017; Manca et al. 2019), which is not always permitted. However, changes to the surface of the object after SERS are not usually noticeable to the naked eye, and recent developments to the technique, by the introduction of a doped gelatine nanocomposite, have meant that even under the microscope, it is impossible to notice any visual modification to the area that has been analysed (Doherty et al. 2011, 2014).

Good results were recently obtained by using fluorescence spectroscopy. This technique, which is also called spectrofluorimetry, has proven to be able to discriminate and identify a number of natural organic dyes and their lakes (Melo 2016; Aceto et al. 2017; Nabais et al. 2018).

[9] http://cameo.mfa.org/wiki/Berberis_dye. Accessed 7 December 2020.

Dyes can usually be fully characterised only if a sample can be taken for chromatographic analysis and destroyed in the process (Analytical Methods Committee, AMCTB No. 101 2021). This is frequently done for textile objects, which often contain sacrificial, loose threads (Burgio 2018; Tamburini 2019; Shahid et al. 2019), but can in principle be extended to manuscripts.

## How to tackle the analysis of inks, pigments and dyes: typical questions

There are countless ways to approach the scientific investigation of a manuscript. Some are surprisingly low tech (a UV torch, a stereomicroscope); others can be bewilderingly complex and involve high-tech equipment and expertise. A separate mention can be made about highly specialised set-ups that are only available in a handful of locations in each country: synchrotron radiation sources allow access to high-energy X-rays with specifications exceeding those provided by conventional instrumentation, and have enhanced the capabilities of many analytical techniques (Cotte et al. 2018). However, the objects have to go to the synchrotron's location for analysis, which is not always feasible.

Much depends on the questions that are being asked; this section will discuss a selection of common issues and queries, and suggest ways to address them where possible.

### Health and safety: are there any toxic elements?

This is one of the issues that arise very frequently. Many traditional pigments contain toxic elements, such as mercury, arsenic or lead, and new health and safety rules demand that a record of such elements is kept in objects' documentation. The fastest, non-destructive way of establishing the presence of hazardous elements is to use an X-ray fluorescence (XRF) spectrometer (Delbey et al. 2019). There are different types of XRF equipment, but all can be used for this purpose: hand-held or portable units, micro-XRF instruments and scanning spectrometers. All but the last one can be used in a point-and-shoot mode: you choose which spot or which pigment on the page you want to investigate, and within seconds, you get a reading that reveals the elements detected there.

Micro-XRF spectrometers have the best spatial resolution: the more sophisticated equipment can analyse areas that are less than 50 µm across (that is, less than a twentieth of a millimetre); hand-held and portable XRF spectrometers usually have a spot size range of 1–10 mm.

Analyses done with scanning XRF spectrometers are more time-consuming, but provide a map with the

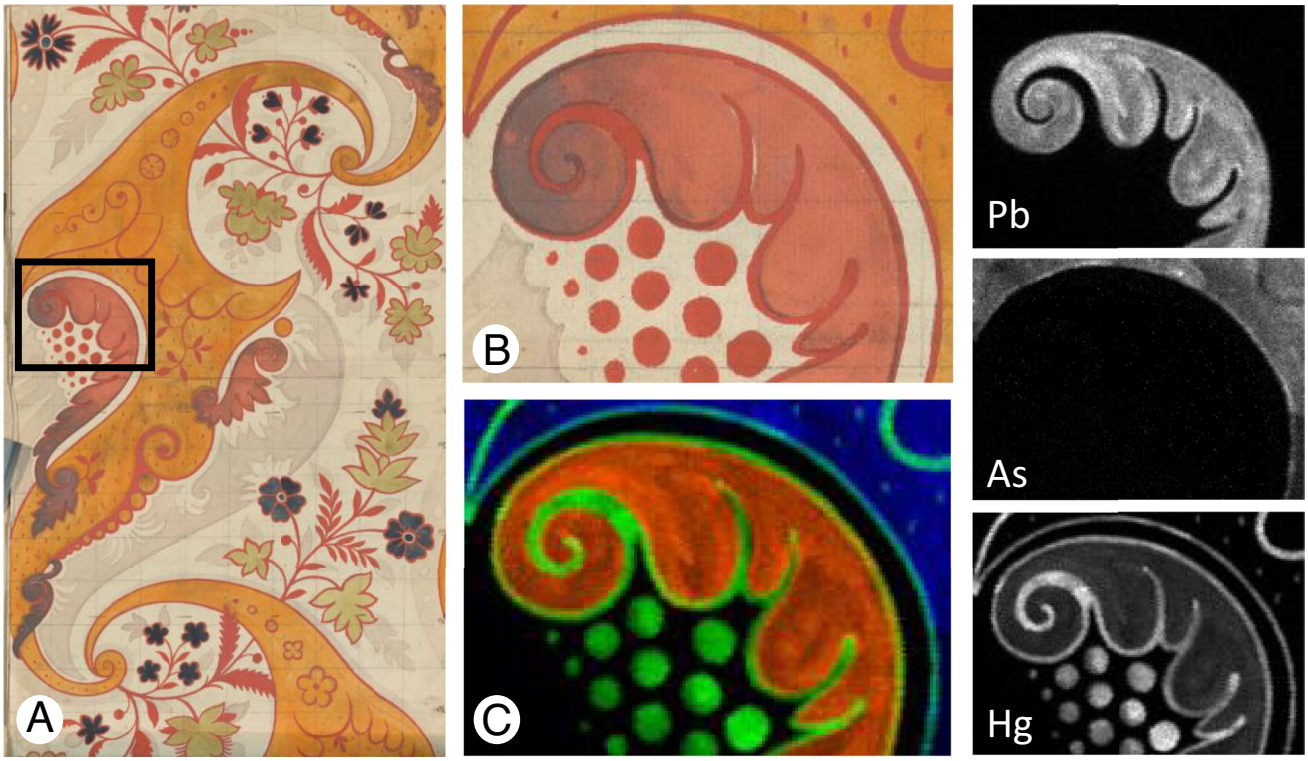


**Fig. 2** How XRF mapping can show the distribution of potentially hazardous materials on a surface: Leman design 89, V&A accession number E.1861:89–1991 (**A**); detail chosen for elemental mapping (**B**); and combination of mercury (green), lead (red) and arsenic (blue) maps (**C**). The three maps in black and white show the individual distribution of each of the three elements. Experiments made in the framework of Iperion-CH grant n. 654,028, see Manca et al. (2019) for the experimental details

distribution of the elements on the whole page—or a portion of the page if this is too large, as in a medieval lectionary. At a glance, you can infer which poisonous pigments may be present and how abundant they are.

Figure 2 shows a design for woven silk created in the early eighteenth century, a small portion of which was analysed by scanning XRF. The resulting elemental maps show the distribution of mercury, lead and arsenic, which appear to be the main constituents of the pigments used on the design. This information can be used, among many other purposes, to inform decisions on the safe handling and storage of the design.

XRF only provides elemental analysis, but does not tell you exactly which particular molecule is present. However, much can be extrapolated using the evidence, i.e. the colour of the area analysed and the elements detected in it, bearing in mind that in many cases, multiple possibilities and pigment/dye combinations can be valid.

If more precise information is needed about the species present in these areas, then other techniques providing molecular identification need to be used, as mentioned in the "Analysis approach: to damage or not to damage?" section.

## Spotting modifications

It is not unusual to be able to see pentimenti, retouchings or later interventions with the naked eye or under a microscope. However, sometimes, these additions are executed so sympathetically that they are difficult to spot. Simple techniques, which are also easily available, can be used first: an ultraviolet lamp and examination by raking light can help to identify areas which may have been reworked (Kimbriel and Ricciardi 2020). Please note that the use of UV lamps needs specific health and safety precautions, for example, the use of safety goggles to protect the eyes of any people present.

Infrared imaging and infrared reflectography can also be used. Both techniques can reveal the presence of pentimenti and retouchings, and can also uncover underdrawings by penetrating through the layers of pigments and dyes (Ricciardi et al. 2013). Interestingly, these techniques can also show if the underdrawing was traced with a dry medium, such a graphite pencil, or a liquid one, as is the case with traditional Chinese underdrawings (Kogou et al. 2015).

However, it is also helpful to have additional tools that delineate the full extent of any modifications on a page or surface. XRF mapping, described in the previous section,

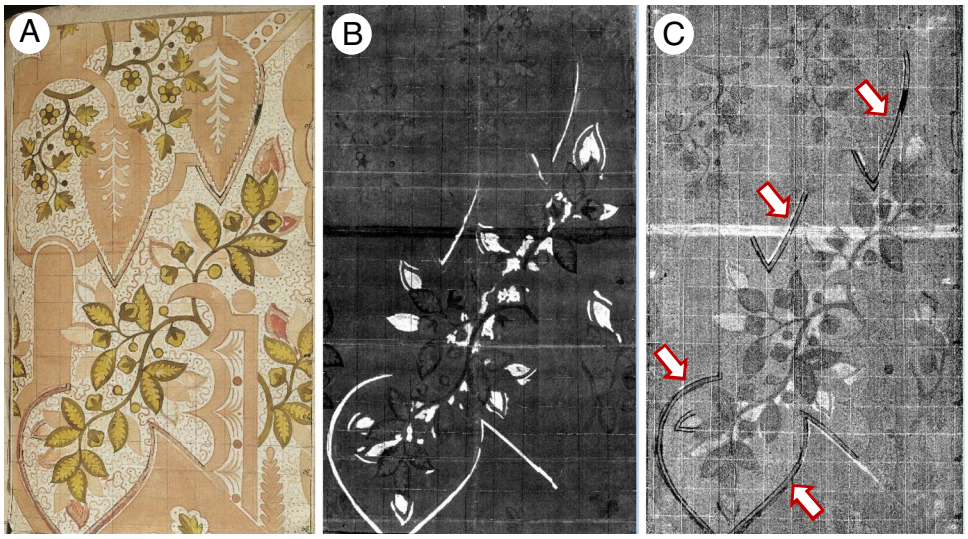


**Fig. 3** (A) Design 73 from the V&A Leman album (accession number E.1861:73–1991) and images created after hyperspectral imaging experiments, emphasising which areas of later interventions have been painted with lead white (**B**) and where a dark ink has been used to outline some of the details (**C**, marked by red arrows). Experiments made in the framework of Iperion-CH grant n. 654,028, see Manca et al. (2019) for the experimental details

can be such a tool, if the materials that have been used for the additional intervention are different from the original ones. It can also complement infrared imaging and multispectral imaging by visualising underdrawings. Underdrawings made with iron-gall ink, metalpoint and pigmented inks can therefore be revealed (Turner et al. 2019). An even better tool is hyperspectral imaging (Melessanaki et al. 2001; Fischer and Kakoulli 2006; Cucci et al. 2016), which has a higher spectral resolution and simultaneously records spectral and spatial information from an object. This information can be displayed in such a way that it shows at a glance the distribution of different materials on a surface, thereby highlighting most alterations. This is the case of the experiments performed on the Leman Album, a group of watercolour designs for woven silk belonging to the V&A collections (Fig. 3, see also Burgio 2017a; Manca et al. 2019).

The characterisation of the modified areas and the identification of the materials in them can be tackled with other techniques, such as Raman microscopy and FTIR. Micro X-ray diffraction (μXRD) is also available, and has been recently used on the non-destructive, in situ analysis of manuscripts (Duran et al. 2009, 2014).

## What type of ink?

As mentioned in a previous section, it is not always straightforward to establish at a glance the composition of writing inks. It is true that iron gall inks are usually browner than carbon-based ones, but on occasions the two types of ink can be visually indistinguishable. Studies under way at Yale show that the amounts of iron, copper and zinc in the ink has a connection with the visual appearance of the ink – the higher the concentration of those elements, the blacker the ink.[10]

[10] Hark RR, personal communication, 2020.

Techniques such as Raman microscopy can fingerprint and unambiguously identify these two inks, with the bonus of being able to detect any additional pigments that may have been included in the ink mixture (for example, Prussian blue in the nineteenth century – this was detected in some of Charles Dickens' autographic manuscripts currently in the V&A collections, see Burgio 2010). FTIR can easily identify iron gall inks (Miliani et al. 2012). Multispectral imaging can also discriminate between the two types of ink, which behave very differently when exposed to infrared radiation: iron gall ink is transparent, carbon-based inks (or pencils) are not, as discussed earlier. This different behaviour is particularly useful when both types of material are present on a page, as shown in Fig. 1: Anything traced with a carbon-based material (the numbers, the grid) is still visible in the infrared, but the iron gall ink handwriting coming through the other side of the page becomes invisible.

## What binding media?

It is normally assumed that the binding media on manuscripts are water based, most commonly gum Arabic, animal glue and occasionally egg (Thompson 1956). Until recently, their non-destructive, in situ identification was deemed to be virtually impossible. However, recent advances have shown that FORS can be used to categorise binding media broadly (Analytical Methods Committee AMCTB No. 75 2016), NIR reflectance imaging spectroscopy can be used to map binders (Dooley et al. 2013), and FTIR can successfully discriminate gum Arabic from egg-based binders (Ricciardi et al. 2012), although there are cases where the pigment present in the mixture may hinder the analysis (Nodari and Ricciardi 2019).

Where minimal sampling is permitted, there are techniques such as matrix-assisted laser desorption/ionization

time-of-flight mass spectrometry (MALDI-TOF–MS) that allow to investigate the degradation processes of binders (Romero-Pastor et al. 2012). Minimal sampling is also sufficient for sophisticated methods such as peptide mass fingerprinting, which can also reliably identify the source of animal protein (both for the investigation of binders and parchment substrates, see Calà et al. 2019; Fiddyment et al. 2015).

### Dating and authenticating

It is essential to state that, on its own, the characterisation of pigments and dyes alone cannot date or authenticate an object. The analysis of the support and of the other materials constituting the object may also help. Crucially, any scientific analysis needs to be supported by technical, curatorial and art historical expertise to evaluate not only the materiality of an object but also its execution and context.

With this premise, the presence of specific materials on a manuscript can be used to infer the date and/or authenticity of the object (Burgio 2012; Nesměrák and Němcová 2012). Many synthetic pigments and dyes introduced from the early eighteenth century have a known first date of manufacture. We are also aware of the geographical origin and approximate time of invention of many older synthetic materials, although in this case we must keep an open mind and be mindful that new evidence may change what we think we know. For example, zinc oxide has traditionally been associated with works from the early nineteenth century onward, but recent evidence has shown that some artists were using it routinely a few decades earlier (Kühn 1986; Houston 2011).

Materials such as Prussian blue can provide a good litmus test: Prussian blue was first discovered in 1704, and became widely available commercially from the 1720s (Berrie 1997). Finding it on a Renaissance illumination may signify that someone has retouched the manuscript after the early eighteenth century, or that the illumination is not from the Renaissance period and is a later imitation (fraudulent or otherwise). A similar argument was made for supposedly medieval miniatures, which were found to contain typically nineteenth-century pigments such as chrome yellow, synthetic ultramarine and emerald green (Burgio et al. 2009b) and purportedly thirteenth-century BCE papyri, whose pigments included twentieth-century materials such as phthalocyanine blue and green, Hansa yellow, titanium white and β-naphthol red (Burgio and Clark 2000). In both cases, the scientific analysis evidence, together with the knowledge and connoisseurship of many specialists, clearly indicated that these objects were not authentic.

A special mention has to be made of modern pigments the composition of which is effectively identical to that of traditional materials used since antiquity: their presence on manuscripts has to be evaluated carefully. Two examples are synthetic haematite (red iron oxide) and synthetic ultramarine blue: chemically speaking, they are effectively indistinguishable from their natural counterparts. However, the morphology and colour distribution of the individual pigment particles—assessed under a high-magnification microscope—does not match that of the natural materials. Synthetic pigment particles tend to be much more uniform in shape, size and hue, and the particle size is usually much smaller than that of the corresponding natural materials. The latter also tend to be accompanied by traces of other substances, with which they occur in nature (Aru et al. 2014): natural ultramarine blue may contain trace amounts of calcite, pyrites and other minerals, while its synthetic version is usually pure, unless it has been deliberately mixed with other materials.

There is a scientific method that can be used for the direct dating of iron gall inks: scanning Auger microscopy (SAM) determines the time elapsed since ink was deposited on the substrate (McNeil 1984; Nesměrák and Němcová 2012). However, there are very few occasions where this capability has been put to good use.

### Linking the dots

The analysis of artists' materials can occasionally help in making connections between different objects, and provide information about their wider context and even their provenance.

Trade routes and commercial relationships can be revealed (Burgio et al. 2009a, b; Bailey 2012; Liang et al. 2014; Kogou et al. 2015), and the geological origin of some of the mineral pigments can be surmised (Schmidt et al. 2009; Smith and Klinshaw 2009; Gambardella et al. 2016), although some of the scientific methods used for this type of investigation may not easily lend themselves to the routine analysis of manuscripts. However, the mapping of trace elements and impurities in naturally sourced pigments for provenancing purposes is still in its infancy and will need to be developed further (Aru et al. 2014; Smieska et al. 2017).

## Analysis protocol

Extracting as much information as possible from a manuscript can be a daunting task: there are so many questions that can be asked and so many different analytical techniques at our disposal to answer them. There is no single technique that can address all questions and a combination of complementary methods and a range of professional skills are often needed. It is also easy to become entangled in endless analyses and to lose track of the overall picture.

Much has been written on the scientific analysis of manuscripts, but most of the literature available tends to focus on

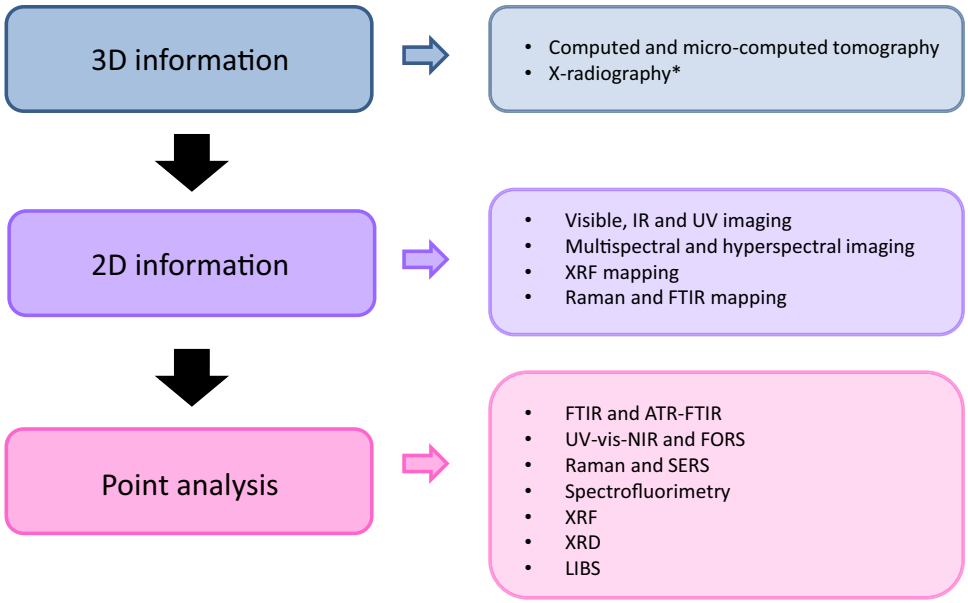


**Fig. 4** Outline of protocol for the scientific analysis of manuscripts. *Please see the main text for additional clarifications on X-radiography

case studies. There have been reviews and protocol suggestions, although they are usually aimed at specialist audiences (Aceto et al. 2012; Pessanha et al. 2012; Ricciardi et al. 2013; Tonazzini et al. 2019). An exception is the 2001 review by Mark Clarke on the scientific methods available for the analysis of manuscripts (Clarke 2001), as well as the soon-to-be-published overview by Ricciardi and Schmidt Patterson (2020).

This section outlines a general analysis protocol for the analysis of manuscripts, not fully exhaustive but covering a range of questions and issues. The protocol can be adapted and modified according to individual needs and circumstances (e.g. the type of object under observation, its specific characteristics and issues, the questions raised about it and the scientific equipment and expertise available), and is made of three main sequential steps that go from a three-dimensional overview of the object as a whole to specific methodologies targeted at a single point or even an individual pigment particle on the object (Fig. 4).

If an overview of the manuscript as a whole is needed, techniques that provide us with three-dimensional information should be used first: computed tomography (or even better, micro-computed tomography, which has higher spatial resolution) is the ideal technique to investigate the structure of a manuscript, and identify any hidden features, such as nails, screws, inserts, internal cracks and so on (see Analytical Methods Committee, AMCTB No. 98 2020). Computed tomography has also proven invaluable when the object cannot be opened or unrolled without risking its integrity, as is the case of ancient scrolls, which can now be unrolled virtually, revealing some of their content (Seales et al. 2011; Rosin et al. 2018; Stromer et al. 2018). However, this is not an easily accessible technique, and very often the most straightforward, practical option is to turn to conventional X-radiography instead. Although X-radiography is capable of retrieving information from a manuscript as a whole object, this information is somewhat 'flattened', and the interpretation of it can turn out to be limited. However, recently developed volumetric radiography systems (e.g. Digitome) can utilise conventional X-ray capabilities and specialised software to create 3D images.[11]

The second step involves the assessment of individual surfaces (a folio, a portion of a scroll). Again, it is a good idea to evaluate the whole surface at a glance, and there are several imaging techniques that can be of use: from low-tech ones such as examination under different types of visible light, as well as infrared and ultraviolet light, to more complex ones such as multispectral and hyperspectral imaging (Liang 2011), and other types of spectroscopic mapping. As explained above, these methods provide evidence about the distribution of specific materials and their mixtures on a page, can help to identify areas that were modified and provide the necessary, preliminary information to select spots that will need to be investigated further. When used within the wider context of connoisseurship and art history, these imaging techniques can also provide information that can assist in the dating, authentication, provenancing and attribution of the objects.

The final step often stems from the second: evidence acquired during the imaging of the object may trigger the investigation of specific areas or individual points of the object. When used in this mode, techniques such as Raman microscopy, FORS and FTIR can answer specific questions

[11] http://licensedigitome.weebly.com/. Accessed 7 December 2020.

about the object, such as the identity of the pigments and binders in specific areas.

Recently, techniques that were conventionally used on small, individual spots have been used in mapping (or imaging) mode, collecting spectral data over larger areas and providing information on the distribution and abundance of specific materials (Ropret et al. 2010; Delaney et al. 2014; Mosca et al. 2016). Examples include FTIR mapping and XRF mapping, which can be used to identify at a glance all the areas that contain hazardous materials such as lead or arsenic; FORS, which can be used to map the distribution of binding media on a folio; and Raman mapping, which can map the distribution of a specific degradation product.

Whether planning a quick test on single objects or a wider analysis campaign, it is important to clarify in advance what the purpose of the study is, and what the main questions are. This will inform the selection and sequence of the relevant protocol steps. Efficiency and economy in the use of the available resources (staff time as well as equipment) should always be considered. There is no point in embarking in a lengthy sequence of complex analyses when a quick, simple series of tests can provide the required answers. It is also crucial to recognise that, while the actual analysis may take a few minutes or hours only, the evaluation of the data may take significantly longer and raise additional questions, paving the way for more analyses and more techniques. It is not unusual that, during perfectly routine and supposedly predictable analyses, researchers may come across unexpected scientific evidence, which in turns leads to new discoveries, as it happened in the case of a number of illuminations by Jean Bourdichon. Two research groups independently discovered that Bourdichon had consistently used an unusual material, metallic bismuth, not only as a paint pigment, but also as a 'pencil' to trace the underdrawing of his miniatures (Trentelman and Turner 2009; Burgio et al. 2009a; Burgio 2017b). This in turn revealed details about medieval trade routes, and paved the way for future attribution and authentication studies.

While the general structure of the analysis protocol may be fixed, the details and the exact sequence of the individual analyses may change, case by case.

## Conclusion

There is no fixed, rigid pathway for the analysis of the materials used on manuscripts. A general protocol can be followed, but this must be adapted to the specific cases and to the questions that are asked about a manuscript or group of manuscripts. While non-invasive, non-destructive techniques are usually preferred, there may be occasions when a more invasive and/or destructive approach is warranted and justifiable. The quality of the data should always be paramount: quickly gathered but inaccurate data should not be preferred to results stemming from longer, more accurate investigations. The involvement of knowledgeable, expert scientists is essential in any investigation of manuscripts, but the contribution from conservators, curators and other specialists is paramount for a truly holistic evaluation of the objects and their materiality, meaning and context.

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## Declarations

**Conflict of interest** The authors declare no competing interests.

## References

Abel A (2012) The history of dyes and pigments: from natural dyes to high performance pigments. In: Colour Design. Woodhead Publishing, pp 557–587. https://doi.org/10.1016/B978-0-08-101270-3.00024-2

Aceto M (2021) The palette of organic colourants in wall paintings. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01392-3

Aceto M, Calà E (2017) Analytical evidences of the use of iron-gall ink as a pigment on miniature paintings. Spectrochim Acta Part A Mol Biomol Spectrosc 187:1–8. https://doi.org/10.1016/j.saa.2017.06.017

Aceto M, Agostino A, Boccaleri E, Garlanda AC (2008) The Vercelli Gospels laid open: an investigation into the inks used to write the oldest Gospels in Latin. X-Ray Spectrometry Int J 37(4):286–292. https://doi.org/10.1002/xrs.1047

Aceto M, Agostino A, Fenoglio G, Gulmini M, Bianco V, Pellizzi E (2012) Non invasive analysis of miniature paintings: proposal for an analytical protocol. Spectrochim Acta Part A Mol Biomol Spectrosc 91:352–359. https://doi.org/10.1016/j.saa.2012.02.021

Aceto M, Agostino A, Fenoglio G, Idone A, Gulmini M et al (2014) Characterisation of colourants on illuminated manuscripts by portable fibre optic UV-visible-NIR reflectance spectrophotometry. Anal Methods 6(5):1488–1500. https://doi.org/10.1039/C3AY41904E

Aceto M, Agostino A, Fenoglio G, Idone A, Crivello F et al (2017) Analytical investigations on the Coronation Gospels manuscript. Spectrochim Acta Part A Mol Biomol Spectrosc 171:213–221. https://doi.org/10.1016/j.saa.2016.07.050

Analytical Methods Committee AMCTB No. 67 (2015) Raman spectroscopy in cultural heritage: Background paper. Anal Methods7: 4844–4847. https://doi.org/10.1039/C5AY90036K. Open access online: https://pubs.rsc.org/az/content/articlepdf/2015/ay/c5ay90036k

Analytical Methods Committee, AMCTB No. 101 (2021) Analysis of historical dyes on heritage objects. Anal Methods. https://doi.org/10.1039/D0AY90167A. Open access online https://pubs.rsc.org/az/content/articlepdf/2021/ay/d0ay90167a

Analytical Methods Committee AMCTB No. 75 (2016) UV-visible-NIR reflectance spectrophotometry in cultural heritage: Background paper. Anal Methods 8: 5894–5896. https://doi.org/10.1039/c6ay90112c. Open access online: https://pubs.rsc.org/en/content/articlepdf/2016/ay/c6ay90112c

Analytical Methods Committee AMCTB No. 80 (2017) Surface-enhanced Raman spectroscopy (SERS) in cultural heritage. Anal Methods 9(30): 4338–4340. https://doi.org/10.1039/C7AY90097J. Open access online: https://www.rsc.org/images/TB_80_tcm18-249824.pdf

Analytical Methods Committee AMCTB No. 91 (2019) Laser-induced breakdown spectroscopy (LIBS) in cultural heritage. Anal Methods 11: 5833–5836. https://doi.org/10.1039/C9AY90147G. Open access online: https://pubs.rsc.org/en/content/articlepdf/2019/ay/c9ay90147g

Analytical Methods Committee, AMCTB No. 98 (2020) X-ray micro computed tomography in cultural heritage. Anal Methods 12(36): 4496–4500. https://doi.org/10.1039/D0AY90112A. Open access online https://pubs.rsc.org/az/content/articlepdf/2020/ay/d0ay90112a

Arizzi A, Cultrone G (2021) Mortars and plasters – How to characterise hydraulic mortars. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01404-2

Aru M, Burgio L, Rumsey MS (2014) Mineral impurities in azurite pigments: artistic or natural selection? J Raman Spectrosc 45(11–12):1013–1018. https://doi.org/10.1002/jrs.4469

Bailey K (2012) A note on Prussian blue in nineteenth-century Canton. Stud Conserv 57(2):116–121. https://doi.org/10.1179/2047058412Y.0000000002

Becker H (2021) Pigment nomenclature in the ancient Near East, Greece, and Rome. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01394-1

Berrie BH (1997) Prussian Blue. In: West FitzHugh E (ed) Artists' Pigments. A Handbook of their History and Characteristics volume 3. National Gallery of Art, Washington. ISBN 0894682563. Open access online: https://www.nga.gov/content/dam/ngaweb/research/publications/pdfs/artists-pigments-vol3.pdf

Berrie BH, editor (2007) Artists' Pigments: Volume 4: A Handbook of their History and Characteristics. Archetype Publications, London. ISBN: 9781904982234

Berrie BH, Matthew LC (2005) Material innovation and artistic invention: new materials and new colors in Renaissance Venetian paintings. In: Scientific Examination of Art: Modern Techniques in Conservation and Analysis. Washington: National Academy Press. Open access online: https://www.nap.edu/read/11413/chapter/3

Bersani D, Conti C, Matousek P, Pozzi F, Vandenabeele P (2016) Methodological evolutions of Raman spectroscopy in art and archaeology. Anal Methods 8(48):8395–8409. https://doi.org/10.1039/C6AY02327D

Brunetti B, Miliani C, Sgamellotti A (2016) MOLAB growth, aims and results. Tech Sci Service De L'histoire De L'art Et De La Préservation Des Biens Culturels 43:32–40. https://doi.org/10.4000/techne.592

Budnar M, Uršič M, Simčič J, Pelicon P, Kolar J, Šelih VS, Strlič M (2006) Analysis of iron gall inks by PIXE. Nucl Instrum Methods Phys Res Sect B 243(2):407–416. https://doi.org/10.1016/j.nimb.2005.10.013

Burgio L (2000) Analysis of pigments on art objects by Raman microscopy and other techniques. Doctoral dissertation, University College London

Burgio L (2010) Victoria and Albert Museum - internal scientific analysis report 10–160-LB

Burgio L (2011) Analysis of Pigments on Manuscripts by Raman Spectroscopy: Advantages and Limitations. In: Neate S, Howell D, Ovenden R, Pollard AM (eds) The technological study of books and manuscripts as artefacts: research questions and analytical solutions. Archeopress, pp 67–76. ISBN 978 1 4073 0767 1

Burgio L (2012) Study of Manuscripts by Vibrational Spectroscopy. In: Edwards HGM, Chalmers JM (eds) Infrared and Raman Spectroscopy in Forensic Science. Wiley, pp 409–417

Burgio L (2017a) James Leman's glorious palette – part 3, https://www.vam.ac.uk/blog/caring-for-our-collections/james-lemans-glorious-palette-part-3. Accessed 7 Dec 2020

Burgio L (2017b) A prayer book fit for a king. https://www.vam.ac.uk/blog/caring-for-our-collections/a-prayer-book-fit-for-a-king. Accessed 7 Dec 2020

Burgio L (2018) Dye analysis of the psychedelic Leman silk. https://www.vam.ac.uk/blog/caring-for-our-collections/dye-analysis-of-the-psychedelic-leman-silk. Accessed 7 Dec 2020

Burgio L (2019) Nonsuch Palace: a Tudor Grand Design? https://www.vam.ac.uk/blog/museum-life/nonsuch-palace-a-tudor-grand-design. Accessed 7 Dec 2020

Burgio L, Clark RJH (2000) Comparative pigment analysis of six modern Egyptian papyri and an authentic one of the 13th century BC by Raman microscopy and other techniques. J Raman Spectrosc 31(5):395–401. https://doi.org/10.1002/1097-4555(200005)31:5%3c395::AID-JRS527%3e3.0.CO;2-E

Burgio L, Clark RJH (2001) Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation. Spectrochim Acta Part A Mol Biomol Spectrosc 57(7):1491–1521. https://doi.org/10.1016/S1386-1425(00)00495-9

Burgio L, Clark RJH, Hark RR (2010) Raman microscopy and x-ray fluorescence analysis of pigments on medieval and Renaissance Italian manuscript cuttings, PNAS 107 (13):, 5726–5731. https://doi.org/10.1073/pnas.0914797107. Open access online: https://www.pnas.org/content/107/13/5726

Burgio L, Bioletti S, Mehan B (2013) Non-destructive, in situ analysis of three early medieval manuscripts from Trinity College Library Dublin (Codex Usserianus Primus, Book of Durrow, Book of Armagh). In: Making Histories: Proceedings of the Sixth International Conference on Insular Art, York 2011

Burgio L, Clark RJH, Hark RR, Rumsey MS, Zannini C (2009a) Spectroscopic investigations of Bourdichon miniatures: masterpieces of light and color. Appl Spectrosc 63(6):611–620. https://doi.org/10.1366/000370209788559593

Burgio L, Clark RJH, Hark RR (2009b) Spectroscopic investigation of modern pigments on purportedly medieval miniatures by the 'Spanish Forger.' J Raman Spectrosc 40(12):2031–2036. https://doi.org/10.1002/jrs.2364

Calà E, Agostino A, Fenoglio G, Capra V, Porticelli F, Manzari F et al (2019) The Messale Rosselli: Scientific investigation on an outstanding 14th century illuminated manuscript from Avignon. J Archaeol Sci Rep 23:721–730. https://doi.org/10.1016/j.jasrep.2018.12.001

Cameo materials database: http://cameo.mfa.org/wiki/Category:Materials_database. Accessed 7 Dec 2020

Cañamares MV, Reagan DA, Lombardi JR, Leona M (2014) TLC-SERS of mauve, the first synthetic dye. J Raman Spectrosc 45(11–12):1147–1152. https://doi.org/10.1002/jrs.4508

Cardon D (2007) Natural dyes. Archetype Publications, London

Caroselli M, Ruffolo SA, Piqué F (2021) Mortars and plasters – How to manage mortars and plasters conservation. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01409-x

Castro R, Pozzi F, Leona M, Melo MJ (2014) Combining SERS and microspectrofluorimetry with historically accurate reconstructions for the characterization of lac dye paints in medieval manuscript illuminations. J Raman Spectrosc 45(11–12):1172–1179. https://doi.org/10.1002/jrs.4608

Cavallo G, Riccardi MP (2021) Glass-based pigments in painting. Archaeol Anthropol Sci (forthcoming)

Cesaratto A, Centeno SA, Lombardi JR, Shibayama N, Leona M (2017) A complete Raman study of common acid red dyes: application to the identification of artistic materials in polychrome prints. J Raman Spectrosc 48(4):601–609. https://doi.org/10.1002/jrs.5082

Chaplin TD, Clark RJH, Jacobs D, Jensen K, Smith GD (2005) The Gutenberg Bibles: analysis of the illuminations and inks using Raman spectroscopy. Anal Chem 77(11):3611–3622. https://doi.org/10.1021/ac050346y

Christiansen T, Buti D, Dalby KN, Lindelof PE, Ryholt K, Vila A (2017) Chemical characterization of black and red inks inscribed on ancient Egyptian papyri: the Tebtunis temple library. J Archaeol Sci Rep 14:208–219. https://doi.org/10.1016/j.jasrep.2017.05.042

Clark RJH (2005) Raman microscopy in the identification of pigments on manuscripts and other artwork. The Scientific Examination of Art. National Academies of Science, Washington, pp 162–185

Clarke M (2001) The analysis of medieval European manuscripts. Stud Conserv 46(sup1):3–17. https://doi.org/10.1179/sic.2001.46.Supplement-1.3

Corregidor V, Viegas R, Ferreira LM, Alves LC (2019) Study of Iron Gall Inks, Ingredients and Paper Composition Using Non-Destructive Techniques. Heritage 2(4):2691–2703. https://doi.org/10.3390/heritage2040166

Cotte M, Genty-Vincent A, Janssens K, Susini J (2018) Applications of synchrotron X-ray nano-probes in the field of cultural heritage. C R Phys 19(7):575–588. https://doi.org/10.1016/j.crhy.2018.07.002

Coupry C, Sagon G, Gorguet-Ballesteros P (1997) Raman spectroscopic investigation of blue contemporary textiles. J Raman Spectrosc 28(2–3):85–89. https://doi.org/10.1002/(SICI)1097-4555(199702)28:2/3%3c85::AID-JRS64%3e3.0.CO;2-4

Craddock P (2009) Scientific investigation of copies, fakes and forgeries. Elsevier

Crippa M, Legnaioli S, Kimbriel C, Ricciardi P (2020) New evidence for the intentional use of calomel as a white pigment. J Raman Spectrosc. https://doi.org/10.1002/jrs.5876

Cucci C, Delaney JK, Picollo M (2016) Reflectance hyperspectral imaging for investigation of works of art: old master paintings and illuminated manuscripts. Acc Chem Res 49(10):2070–2079. https://doi.org/10.1021/acs.accsounts.6b00048

Del Carmine P, Giuntini L, Hooper W, Lucarelli F, Mandò PA (1996) Further results from PIXE analysis of inks in Galileo's notes on motion. Nucl Inst Methods Phys Res B 113:354–358

DeLaine J (2021) Production, transport and on-site organisation of Roman mortars and plasters. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01401-5

Delaney JK, Ricciardi P, Glinsman LD, Facini M, Thoury M, Palmer M, de la Rie ER (2014) Use of imaging spectroscopy, fiber optic reflectance spectroscopy, and X-ray fluorescence to map and identify pigments in illuminated manuscripts. Stud Conserv 59(2):91–101. https://doi.org/10.1179/2047058412Y.0000000078

Delbey T, Holck JP, Jørgensen B, Alvis A, Smith VH, Kavich GM et al (2019) Poisonous books: analyses of four sixteenth and seventeenth century book bindings covered with arsenic rich green paint. Heritage Science 7(1):91. https://doi.org/10.1186/s40494-019-0334-2

Di Stefano LM, Fuchs R (2011) Characterisation of the pigments in a Ptolemaic Egyptian Book of the Dead papyrus. Archaeol Anthropol Sci 3(3):229. https://doi.org/10.1007/s12520-011-0054-3

Doherty B, Brunetti BG, Sgamellotti A, Miliani C (2011) A detachable SERS active cellulose film: a minimally invasive approach to the study of painting lakes. J Raman Spectrosc 42(11):1932–1938. https://doi.org/10.1002/jrs.2942

Doherty B, Daveri A, Clementi C, Romani A, Bioletti S, Brunetti B et al (2013) The Book of Kells: a non-invasive MOLAB investigation by complementary spectroscopic techniques. Spectrochim Acta Part A Mol Biomol Spectrosc 115:330–336. https://doi.org/10.1016/j.saa.2013.06.020

Doherty B, Presciutti F, Sgamellotti A, Brunetti BG, Miliani C (2014) Monitoring of optimized SERS active gel substrates for painting and paper substrates by unilateral NMR profilometry. J Raman Spectrosc 45(11–12):1153–1159. https://doi.org/10.1002/jrs.4542

Domingo Sanz I, Chieli A (2021) Characterising the pigments and paints of prehistoric artists. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01397-y

Dooley KA, Lomax S, Zeibel JG, Miliani C, Ricciardi P, Hoenigswald A et al (2013) Mapping of egg yolk and animal skin glue paint binders in Early Renaissance paintings using near infrared reflectance imaging spectroscopy. Analyst 138(17):4838–4848. https://doi.org/10.1039/C3AN00926B

Douma M (2008) Pigments through the Ages. *Institute for Dynamic Educational Development (IDEA)*. Open access online: www.webexhibits.org/pigments. Accessed 7 Dec 2020

Duran A, Perez-Rodriguez JL, Espejo T, Franquelo ML, Castaing J, Walter P (2009) Characterization of illuminated manuscripts by laboratory-made portable XRD and micro-XRD systems. Anal Bioanal Chem 395(7):1997–2004. https://doi.org/10.1007/s00216-009-2992-5

Durán A, Franquelo ML, Centeno MA, Espejo T, Perez-Rodriguez JL (2011) Forgery detection on an Arabic illuminated manuscript by micro-Raman and X-ray fluorescence spectroscopy. J Raman Spectrosc 42(1):48–55. https://doi.org/10.1002/jrs.2644

Duran A, López-Montes A, Castaing J, Espejo T (2014) Analysis of a royal 15th century illuminated parchment using a portable XRF–XRD system and micro-invasive techniques. J Archaeol Sci 45:52–58. https://doi.org/10.1016/j.jas.2014.02.011

Eastaugh N, Walsh V, Chaplin T, Siddall R (2007) *Pigment compendium: a dictionary of historical pigments*. Routledge. Free pdf available on https://www.researchgate.net/publication/273692562_Pigment_Compendium_A_Dictionary_and_Optical_Microscopy_of_Historic_Pigments

Edwards HGM (2018) Analytical Raman Spectroscopy of Inks. In Raman Spectroscopy in Archaeology and Art History: Volume 2, 1–15. https://doi.org/10.1039/9781788013475-00001

Ergenç D, Fort R, Varas−Muriel MJ, Alvarez de Buergo M, (2021) Mortars and plasters – How to characterise aerial mortars and plasters. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01398-x

Feller R, editor (1986) Artists' Pigments: Volume 1: A Handbook of their History and Characteristics. National Gallery of Art, Washington. Open access online: https://www.nga.gov/content/dam/ngaweb/research/publications/pdfs/artists-pigments-vol1.pdf

Fiddyment S, Holsinger B, Ruzzier C, Devine A, Binois A, Albarella U et al (2015) Animal origin of 13th-century uterine vellum revealed using noninvasive peptide fingerprinting. Proc Natl Acad Sci 112(49):15066–15071. https://doi.org/10.1073/pnas.1512264112

Fischer C, Kakoulli I (2006) Multispectral and hyperspectral imaging technologies in conservation: current research and potential applications. Stud Conserv 51(sup1):3–16. https://doi.org/10.1179/sic.2006.51.Supplement-1.3

Flieder F (1968) Mise au point des techniques d'identification des pigments et des liants inclus dans la couche picturale des enluminures de manuscrits. Stud Conserv 13(2):49–86. https://doi.org/10.1179/sic.1968.005

Ford B (2018) A microfading survey of the lightfastness of blue, black and red ballpoint pen inks in ambient and modified environments. AICCM Bull 39(1):26–34. https://doi.org/10.1080/10344233.2018.1515809

Gambardella AA, Schmidt Patterson CM, Webb SM, Walton MS (2016) Sulfur K-edge XANES of lazurite: Toward determining the provenance of lapis lazuli. Microchem J 125:299–307. https://doi.org/10.1016/j.microc.2015.11.030

Gettens RJ, Kuhn H, Chase WT (1993a) Lead White. In Roy A (ed) Artists' Pigments: A Handbook of their History and Characteristics. Volume 2. National Gallery of Art, Washington. Open access online: https://www.nga.gov/content/dam/ngaweb/research/publications/pdfs/artists-pigments-vol1.pdf

Gettens RJ, Feller R, Chase W (1993b) Vermilion and Cinnabar. In Roy A (ed) Artists' Pigments: A Handbook of their History and Characteristics. Volume 2. National Gallery of Art, Washington. Open access online: https://www.nga.gov/content/dam/ngaweb/research/publications/pdfs/artists-pigments-vol1.pdf

Gliozzo E (2021) Pigments – Mercury-based red (cinnabar-vermilion) and white (calomel) and their degradation products. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01402-4

Gliozzo E, Burgio L (2021) Pigments – Arsenic-based yellows and reds. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01431-z

Gliozzo E, Ionescu C (2021) Pigments – Lead-based whites, reds, yellows and oranges and their alteration phases. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01407-z

Gliozzo E, Pizzo A, La Russa MF (2021) Mortars, plasters and pigments - Research questions and sampling criteria. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01393-2

Goler S, Hagadorn A, Ratzan DM, Bagnall R, Cacciola A, McInerney J, Yardley JT (2019) Using Raman spectroscopy to estimate the dates of carbon-based inks from Ancient Egypt. J Cult Herit 38:106–117. https://doi.org/10.1016/j.culher.2018.12.003

Grazia C, Buti D, Cartechini L, Rosi F, Gabrieli F, Lladó-Buisán VM et al (2018) Exploring the materiality of Mesoamerican manuscripts by non-invasive spectroscopic methods: Codex Laud, Bodley, Selden, Mendoza and Selden Roll at the Bodleian Library. In: Mesoamerican Manuscripts. Brill, pp 134–159. https://doi.org/10.1163/9789004388116_007

Hahn O (2010) Analyses of iron gall and carbon inks by means of X-ray fluorescence analysis: a non-destructive approach in the field of archaeometry and conservation science. Restaurator Int J Preserv Library Arch Mater 31(1):41–64. https://doi.org/10.1515/rest.2010.003

Harley RD (1982) Artists' pigments, c. 1600–1835; a study in English documentary sources. Butterworth Scientific, London

Hidalgo RJD, Córdoba R, Nabais P, Silva V, Melo MJ, Pina F et al (2018) New insights into iron-gall inks through the use of historically accurate reconstructions. Heritage Sci 6(1):63. https://doi.org/10.1186/s40494-018-0228-8

Houston K (2011) Spectroscopic Analysis of Pigments on Portrait Miniatures by William Wood (1769-1810). Undergraduate dissertation, Juniata College, Pennsylvania

Kimbriel C, Ricciardi P (2020) Secrets of a Silent Miniaturist: Findings from a Technical Study of Miniatures Attributed to Isaac Oliver. British Art Studies, (17). https://doi.org/10.17658/issn.2058-5462/issue-17/kimbrielricciardi. Open access online https://doi.org/10.17658/issn.2058-5462/issue-17/kimbrielricciardi

Knapp CW, Christidis GE, Venieri D, Gounaki I, Gibney-Vamvakari J, Stillings M, Photos-Jones E (2021) The ecology and bioactivity of some Greco-Roman medicinal minerals: the case of Melos earth pigments. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01396-z

Kogou S, Lucian A, Bellesia S, Burgio L, Bailey K, Brooks C, Liang H (2015) A holistic multimodal approach to the non-invasive analysis of watercolour paintings. Appl Phys A 121(3):999–1014. https://doi.org/10.1007/s00339-015-9425-4

Kühn H (1986) Zinc white. In: Roy A (ed) Artists' Pigments: A Handbook of their History and Characteristics. Volume 2. National Gallery of Art, Washington. Open access online: https://www.nga.gov/content/dam/ngaweb/research/publications/pdfs/artists-pigments-vol1.pdf

Kühn H (1993) Verdigris and Copper Resinate. In: Roy A (ed) Artists' Pigments: A Handbook of their History and Characteristics. Volume 2. National Gallery of Art, Washington. Open access online: https://www.nga.gov/research/publications/pdf-library/artists-pigments-vol2.html

La Russa MF, Ruffolo SA (2021) Mortars and plasters - How to characterise mortars and plasters degradation. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01405-1

Lancaster LC (2021) Mortars and plasters – How mortars were made. The Literary Sources. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01395-0

Leach B, Tait WJ (2000) Papyrus. In: Nicholson PT, Shaw I (eds) Ancient Egyptian Materials and Technology. University Press, Cambridge, pp 227–253

Lee AS, Mahon PJ, Creagh DC (2006) Raman analysis of iron gall inks on parchment. Vib Spectrosc 41(2):170–175. https://doi.org/10.1016/j.vibspec.2005.11.006

Lee AS, Otieno-Alego V, Creagh DC (2008) Identification of iron-gall inks with near-infrared Raman microspectroscopy. J Raman Spectrosc 39(8):1079–1084. https://doi.org/10.1002/jrs.1989

Leona M, Winter (2001) Fiber optics reflectance spectroscopy: a unique tool for the investigation of Japanese paintings. Stud Conserv 46(3):153–162. https://doi.org/10.1179/sic.2001.46.3.153

Liang H (2011) Advanced optical imaging methods for investigating manuscripts. In: Neate S, Howell D, Ovenden R, Pollard AM (eds) The technological study of books and manuscripts as artefacts: research questions and analytical solutions. Archaeopress, Oxford, pp 55–66 (**ISBN 9781407307671**)

Liang H, Burgio L, Bailey K, Lucian A, Dilley C, Bellesia S, Cheung C, Brooks C (2014) Culture and trade through the prism of technical art history: A study of Chinese export paintings. Stud Conserv 59(sup1):S96–S99. https://doi.org/10.1179/204705814X13975704318272

Lucas A (1962) Ancient Egyptian Materials and Industries, 4th ed. Revised by J.R. Harris. London: Edward Arnold

Manca R, Burgio L, Button V et al (2019) Scientific analysis underpinning the multidisciplinary project "The Leman Album: an Enhanced Facsimile." Eur Phys J plus 134:267. https://doi.org/10.1140/epjp/i2019-12668-0

Mastrotheodoros GP, Beltsios KG, Bassiakos Y (2021) Pigments – Iron-based red, yellow and brown ochres. Archaeol Anthropol Sci (forthcoming)

McNeil RJ (1984) Scanning Auger microscopy for dating of manuscript inks. In: Lambert JB (ed) Archaeological Chemistry III. American Chemical Society, Washington, pp 255–269

Melessanaki K, Papadakis V, Balas C, Anglos D (2001) Laser induced breakdown spectroscopy and hyper-spectral imaging analysis of pigments on an illuminated manuscript. Spectrochim Acta Part B 56(12):2337–2346. https://doi.org/10.1016/S0584-8547(01)00302-0

Melo MJ (2009) History of natural dyes in the ancient mediterranean world. In: Bechtold T, Mussak R (eds) Handbook of natural colorants. Wiley, pp 3–20

Melo MJ, Nabais P, Guimarães M, Araújo R, Castro R, Oliveira MC, Whitworth I (2016) Organic dyes in illuminated manuscripts: a unique cultural and historic record. Philos Trans R Soc A Math Phys Eng Sci 374(2082): 20160050. https://doi.org/10.1098/rsta.2016.0050. Available on line: https://royalsocietypublishing.org/doi/pdf/https://doi.org/10.1098/rsta.2016.0050

Melo MJ, Nabais P, Araújo R, Vitorino T (2019) The conservation of medieval manuscript illuminations: A chemical

perspective. *Phys Sci Rev*, *4*(8). https://doi.org/10.1515/psr-2018-0017

Miliani C, Rosi F, Brunetti BG, Sgamellotti A (2010) In situ noninvasive study of artworks: the MOLAB multitechnique approach. Acc Chem Res 43(6):728–738. https://doi.org/10.1021/ar100010t

Miliani C, Rosi F, Daveri A, Brunetti BG (2012) Reflection infrared spectroscopy for the non-invasive in situ study of artists' pigments. Appl Phys A 106(2):295–307. https://doi.org/10.1007/s00339-011-6708-2

Mosca S, Alberti R, Frizzi T, Nevin A, Valentini G, Comelli D (2016) A whole spectroscopic mapping approach for studying the spatial distribution of pigments in paintings. Appl Phys A 122(9):815. https://doi.org/10.1007/s00339-016-0345-8

Murat Z (2021) Wall paintings through the ages. The medieval period (Italy, 12th-15th century). Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01410-4

Mühlethaler B, Thyssen J (1993) Smalt. In: Roy A (ed) Artists' Pigments: A Handbook of their History and Characteristics. Volume 2. National Gallery of Art, Washington, pp 113–130. Open access online: https://www.nga.gov/content/dam/ngaweb/research/publications/pdfs/artists-pigments-vol1.pdf

Nabais P, Melo Maria J, Lopes JA, Vitorino T, Neves A, Castro R (2018) Microspectrofluorimetry and chemometrics for the identification of medieval lake pigments. Heritage Science 6(1). https://doi.org/10.1186/s40494-018-0178-1

Nesměrák K, Němcová I (2012) Dating of historical manuscripts using spectrometric methods: a mini-review. Anal Lett 45(4):330–344. https://doi.org/10.1080/00032719.2011.644741

Nicholson CE, Beeby A, Gameson R (2016) Shedding light on medieval manuscripts. Spectrosc Europe 28(4): 6–8, open access online https://www.spectroscopyeurope.com/system/files/pdf/SE%2028-4-Raman.pdf

Nodari L, Ricciardi P (2019) Non-invasive identification of paint binders in illuminated manuscripts by ER-FTIR spectroscopy: a systematic study of the influence of different pigments on the binders' characteristic spectral features. Heritage Sci 7(1): 7. https://doi.org/10.1186/s40494-019-0249-y. Open access online: https://heritagesciencejournal.springeropen.com/track/pdf/https://doi.org/10.1186/s40494-019-0249-y.pdf

Olsson AM, Calligaro T, Colinart S, Dran JC, Lövestam NEG, Moignard B, Salomon J (2001) Micro-PIXE analysis of an ancient Egyptian papyrus: Identification of pigments used for the "Book of the Dead." Nucl Instrum Methods Phys Res Sect B 181(1–4):707–714. https://doi.org/10.1016/S0168-583X(01)00545-6

Pérez-Arantegui J (2021) Not only wall paintings – Pigments for cosmetics. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01399-w

Pessanha S, Manso M, Carvalho ML (2012) Application of spectroscopic techniques to the study of illuminated manuscripts: a survey. Spectrochim Acta Part B 71:54–61. https://doi.org/10.1016/j.sab.2012.05.014

Pozzi F, Lombardi JR, Leona M (2013) Winsor & Newton original handbooks: a surface-enhanced Raman scattering (SERS) and Raman spectral database of dyes from modern watercolor pigments. Heritage Sci 1(1): 23. https://doi.org/10.1186/2050-7445-1-23. Open access online: https://link.springer.com/article/https://doi.org/10.1186/2050-7445-1-23#Abs1

Pouyet E, Devine S, Grafakos T, Kieckhefer R, Salvant J, Smieska L et al (2017) Revealing the biography of a hidden medieval manuscript using synchrotron and conventional imaging techniques. Anal Chim Acta 982:20–30. https://doi.org/10.1016/j.aca.2017.06.016

Pretzel P (2021) Surface alteration of Japanese lacquers on exposure to (UV-free) light. In: Bridgland J (ed) Transcending Boundaries: Integrated Approaches to Conservation. ICOM-CC 19th Triennial Conference Preprints, Beijing, 17-21 May 2021. International Council of Museums, Paris

Ricciardi P, Delaney JK, Facini M, Zeibel JG, Picollo M, Lomax S, Loew M (2012) Near infrared reflectance imaging spectroscopy to map paint binders in situ on illuminated manuscripts. Angew Chem Int Ed 51(23):5607–5610. https://doi.org/10.1002/anie.201200840

Ricciardi P, Schmidt Patterson C (2020) Science of the book: analytical methods for the study of illuminated manuscripts. In: Panayotova S (ed) A handbook of the art and science of illuminated manuscripts. Harvey Miller, London

Ricciardi P, Delaney JK, Facini M, Glinsman L (2013) Use of imaging spectroscopy and in situ analytical methods for the characterization of the materials and techniques of 15th century illuminated manuscripts. J Am Inst Conserv 52(1):13–29. https://doi.org/10.1179/0197136012Z.0000000004

Ricciardi P, Mazzinghi A, Legnaioli S, Ruberto C, Castelli L (2019) The choir books of San Giorgio Maggiore in Venice: results of in depth non-invasive analyses. Heritage 2(2): 1684–1701. https://doi.org/10.3390/heritage2020103. Open access online: https://www.mdpi.com/2571-9408/2/2/103

Roberts CH, Skeat TC (1983) The birth of the codex. The British Academy, London, pp 15–22

Romero-Pastor J, Navas N, Kuckova S, Rodríguez-Navarro A, Cardell C (2012) Collagen-based proteinaceous binder-pigment interaction study under UV ageing conditions by MALDI-TOF-MS and principal component analysis. Journal of Mass Spectrometry 47(3):322–330. https://doi.org/10.1002/jms.2966

Ropret P, Miliani C, Centeno SA, Tavzes Č, Rosi F (2010) Advances in Raman mapping of works of art. J Raman Spectrosc 41(11):1462–1467. https://doi.org/10.1002/jrs.273

Rosin PL, Lai YK, Liu C, Davis GR, Mills D, Tuson G, Russell Y (2018) Virtual recovery of content from X-ray micro-tomography scans of damaged historic scrolls. Sci Rep 8(1): 1–10. https://doi.org/10.1038/s41598-018-29037-x. Open access online: https://www.nature.com/articles/s41598-018-29037-x

Roy A, editor (1993) Artists' Pigments: Volume 2: A Handbook of their History and Characteristics. National Gallery of Art, Washington. Open access online: https://www.nga.gov/content/dam/ngaweb/research/publications/pdfs/artists-pigments-vol2.pdf

Salvadori M, Sbrolli C (2021) Wall paintings through the ages. The Roman period: Republic and early Empire. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01411-3

Schmidt CM, Walton MS, Trentelman K (2009) Characterization of lapis lazuli pigments using a multitechnique analytical approach: implications for identification and geological provenancing. Anal Chem 81(20):8513–8518. https://doi.org/10.1021/ac901436g

Schweppe H, Winter J (1997) Madder and Alizarin. In: West FitzHugh E (ed) Artists' Pigments. A Handbook of their History and Characteristics' volume 3. National Gallery of Art, Washington. ISBN 0894682563. Open access online: https://www.nga.gov/content/dam/ngaweb/research/publications/pdfs/artists-pigments-vol3.pdf

Scott DA (2016) A review of ancient Egyptian pigments and cosmetics. Stud Conserv 61(4):185–202. https://doi.org/10.1179/2047058414Y.0000000162

Seales WB, Griffioen J, Baumann R, Field M (2011) Analysis of Herculaneum papyri with x-ray computed tomography. In *International Conference on nondestructive investigations and microanalysis for the diagnostics and conservation of cultural and environmental heritage*. Open access online: https://www.ndt.net/article/art2011/papers/FIELD%20-%20M%2014.pdf

Senesi GS, Harmon RS, Hark RR (2020) Field-portable and handheld LIBS: Historical review, current status and future prospects. Spectrochim Acta Part B Atom Spectrosc: 106013. https://doi.org/10.1016/j.sab.2020.106013

Shahid M, Wertz J, Degano I, Aceto M, Khan MI, Quye A (2019) Analytical methods for determination of anthraquinone dyes in historical textiles: A review. Anal Chim Acta 1083:58–87. https://doi.org/10.1016/j.aca.2019.07.009

Siddall R (2018) Mineral pigments in archaeology: their analysis and the range of available materials. Minerals 8(5): 201. https://doi.org/10.3390/min8050201. Open access online: https://www.mdpi.com/2075-163X/8/5/201

Smieska LM, Mullett R, Ferri L, Woll AR (2017) Trace elements in natural azurite pigments found in illuminated manuscript leaves investigated by synchrotron x-ray fluorescence and diffraction mapping. Appl Phys A 123(7):484. https://doi.org/10.1007/s00339-017-1093-0

Smith GD, Klinshaw RJ II (2009) The presence of trapped carbon dioxide in lapis lazuli and its potential use in geo-sourcing natural ultramarine pigment. J Cult Herit 10(3):415–421. https://doi.org/10.1016/j.culher.2008.12.001

Striova J, Pampaloni E, Barucci M, Fontana R, Bracci S, Riminesi C, Ragionieri P, Marongiu M (2014) Michelangelo's drawings seen under visible, infrared and X rays. ART'14 11th International Conference, June 11–13 2014, Museo Arqueòlogico Nacional, Madrid

Stromer D, Christlein V, Martindale C et al (2018) (2018) Browsing through sealed historical manuscripts by using 3-D computed tomography with low-brilliance X-ray sources. Sci Rep 8:15335. https://doi.org/10.1038/s41598-018-33685-4. Openaccessonline:doi:10.1038/s41598-018-33685-4

Švarcová S, Hradil D, Hradilová J, Čermáková Z (2021) Pigments – Copper-based greens and blues. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01406-0

Szirmai JA (1999) The Archaeology of medieval bookbinding. Ashgate, p.3. ISBN 0 85967 9047

Tamburini D (2019) Investigating Asian colourants in Chinese textiles from Dunhuang (7th-10th century AD) by high performance liquid chromatography tandem mass spectrometry–Towards the creation of a mass spectra database. Dyes Pigm 163:454–474. https://doi.org/10.1016/j.dyepig.2018.12.025

Thompson DV (1956) The materials and techniques of medieval painting. Courier Corporation

Tonazzini A, Salerno E, Abdel-Salam ZA, Harith MA, Marras L, Botto A et al (2019) Analytical and mathematical methods for revealing hidden details in ancient manuscripts and paintings: A review. J Adv Res 17:31–42. https://doi.org/10.1016/j.jare.2019.01.003

Tournié A, Fleischer K, Bukreeva I, Palermo F, Perino M, Cedola A et al (2019) Ancient Greek text concealed on the back of unrolled papyrus revealed through shortwave-infrared hyperspectral imaging. Sci Adv 5(10). https://doi.org/10.1126/sciadv.aav8936

Trentelman K, Turner N (2009) Investigation of the painting materials and techniques of the late-15th century manuscript illuminator Jean Bourdichon. J Raman Spectrosc 40(5):577–584. https://doi.org/10.1002/jrs.2186

Turner NK, Patterson CS, MacLennan DK, Trentelman K (2019) Visualizing underdrawings in medieval manuscript illuminations with macro-X-ray fluorescence scanning. X-Ray Spectrom 48(4):251–261. https://doi.org/10.1002/xrs.2956

Vermeulen M, Burgio L, Vandeperre N, Driscoll E, Viljoen M, Woo J et al (2020) Beyond the connoisseurship approach: creating a chronology in Hokusai prints using non-invasive techniques and multivariate data analysis. Heritage Sci 8(1):1–13. https://doi.org/10.1186/s40494-020-00406-y

Vitti P (2021) Mortars and masonry - Structural lime and gypsum mortars in Antiquity and Middle Ages. Archaeol Anthropol Sci. https://doi.org/10.1007/s12520-021-01408-y

Wainwright INM, Taylor JM, Harley RD (1986) Lead Antimonate yellow. In: Feller RL (ed) Artists' Pigments. A Handbook of Their History and Characteristics, Volume 1. National Gallery of Art, Washington, pp 219 – 254. Open access online: https://www.nga.gov/content/dam/ngaweb/research/publications/pdfs/artists-pigments-vol3.pdf

West FitzHugh E, editor (1997) Artists' Pigments: Volume 3: A Handbook of their History and Characteristics. National Gallery of Art, Washington. Open access online: https://www.nga.gov/content/dam/ngaweb/research/publications/pdfs/artists-pigments-vol3.pdf

Whitney AV, Van Duyne RP, Casadio F (2006) An innovative surface-enhanced Raman spectroscopy (SERS) method for the identification of six historical red lakes and dyestuffs. J Raman Spectrosc 37(10):993–1002. https://doi.org/10.1002/jrs.1576

Winter J, West FitzHugh E (2007) Pigments based on Carbon. In: Berrie BH (ed) Artists' Pigments, A Handbook of Their History and Characteristics, vol 4. Archetype, London, pp 1–37 (**ISBN 9781904982234**)