Virtual Archaeology of Altered Paintings: Multi-scale Chemical Imaging Tools

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ABSTRACT

Understanding how painted works of art were constructed, layer-by-layer, requires a range of macroscopic and microscopic X-ray and infrared-based analytical methods. Deconstructing complex assemblies of paints by combining *in plane* and *in depth* information provides insight into the details of the entire production process of the art work and on the painting techniques and styles of its maker. The unwanted chemical transformations that some paint pigments undergo are also detectable; these changes can alter the paint's optical properties. Understanding the chemistry behind such paint degradation gives conservators vital clues to counter these effects and is an invaluable asset in protecting these cultural artefacts for future generations

KEYWORDS Paintings, pigment alteration, X-ray fluorescence, Fourier transform infrared, X-ray diffraction,

INTRODUCTION

Starting from pre-historic times, human artists have always felt the urge to depict their surrounding world on various substrates by using coloured materials of different kinds. Historical paintings, such as prehistoric cave paintings, are often called 'windows on the past' and have allowed later generations to imagine how former human societies looked and/or functioned. Historical paintings are, therefore, an enormously valuable part of the cultural legacy we have inherited from past generations.

There is a general belief that paintings are complex but essentially static assemblages of widely different (in)organic materials. However, at, or just below, the seemingly placid surface of these works of art, chemical reactions are taking place that are slowly altering the chemical make-up of the paint layers. While some of these

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reactions are the result of intimate contact between the different materials, they are mainly propelled by external physicochemical factors. Light absorption by coloured substances (molecules) in the ultraviolet (UV) and the visible range is a prime stimulus for reduction–oxidation (redox) reactions. These reactions can lead to spontaneous in situ formation of secondary chemicals that will often differ in their macroscopic properties (colour, volume, porosity) from the original materials. The organic component of a paint (the protein-, saccharide- or lipid/oil-based binding media, organic dyes, etc.) and some of the inorganic components (mostly mineral pigments based on metal ions) may be affected. Another important factor in paint degradation is the often cyclic variation in relative humidity, which causes condensation and re-evaporation of minute moisture droplets within the microporous, age-cracked paint layers. The latter processes can function as miniature galvanic cells where redox reactions occur at the interface between pigment grains, binding medium and water. In addition, phenomena such as crystallization of salts and leaching of metal cations from pigment grains can gradually undermine the mechanical integrity of paint materials. Cycles of condensation/evaporation may also transport secondary alteration compounds towards the surface, leading to the formation of weathering crusts. These crusts can be partly crystalline and almost all have a colour and texture that is quite different from the original material.

Traditionally, to study the chemical make-up of painted artworks in detail, (minute) paint samples are collected. These tiny samples can be taken using five standard ‘microdestructive’ techniques: scalpels or lancets (e.g. Colombini and Modugno 2004); gentle cotton bud (Q-tip) abrasion (e.g. Vandenabeele et al. 1999); microdrilling (involving a 100–200 µm diameter bore) (e.g. Wess et al. 2004); or laser ablation, the ablated materials being collected on microscope slides (e.g. Cesaratto et al. 2014). These techniques remove only minute amounts of material and any damage is effectively invisible to the naked eye.

Microdestructive sampling is limited, as much as possible, to areas where paint loss has already occurred. The extracted material often comprises the entire stack of micrometre-thick paint layers at a given position. One or more non-destructive micro-analytical methods may be employed before undertaking additional analytical investigations that might involve the chemical digestion of the sampled material, or any other wet-chemical operation. Prior to microanalysis, multilayered paint samples are typically embedded in resin, cross-sectioned and then polished. Alternatively, the

different materials/layers in a paint sample may be carefully separated from each other under the microscope for separate analysis.

The range of analytical techniques available to painting researchers is now fairly extensive and the methods can be used to characterize a painting's materials in detail. They include the following: optical microscopy (OM); scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDX) (Antunes et al. 2014); micro-Fourier transform infrared spectroscopy (μ -FTIR) (Lluveras et al. 2008); micro-Raman spectrometry (μ -RS) (Bell et al. 1997; Van Der Snickt et al. 2008); gas chromatography coupled with mass spectrometry (GCMS); and pyrolysis GCMS (Py-GCMS) (Andreotti et al. 2006; Colombini et al. 2010). To complement these chemical analytical methods there are chemical imaging techniques such as synchrotron radiation (SR)-based micro-X-ray fluorescence (μ -XRF) (Janssens et al. 2000), micro-X-ray absorption near-edge spectroscopy (μ -XANES) (Cotte et al. 2010), micro-X-ray powder diffraction (μ -XRPD) (De Nolf et al. 2010), and synchrotron radiation micro-Fourier transform infrared spectroscopy (SR- μ -FTIR). Often, combinations of these methods are required to fully understand the paints' chemistry (Bertrand et al. 2012; Janssens et al. 2014). A comprehensive understanding of the paints used in a work of art requires data from across the painting's surface, as well as depth profiles through the paint layers themselves. To complement the detailed information that can be gathered from the small number of (possibly non-representative) paint cross sections, mobile versions of different non-destructive spectroscopic methods are used to investigate a greater number of locations on an artwork. By means of a portable XRF (PXRF), element signatures can be swiftly recorded from all differently coloured areas of a painting, allowing indirect inferences to be made on which pigments were used throughout. Similarly, portable RS and FTIR probes can be used to collect complementary vibrational data and so assess the presence of any organic constituents (e.g. Miliani et al. 2010). More recently, several non-invasive imaging methods have been developed and successfully employed to document the composition of a *complete* painting (Daddara et al, 2005; Alfeld et al., 2011; Delaney et al., 2014). They can be considered the state-of-the-art equivalents of the two imaging methods that have been routinely employed in subsurface investigation of paintings for several decades: infrared reflectography (IRR) and X-ray radiography (XRR). Some of these exploit a scanning mode of operation and include the techniques of macroscopic X-ray fluorescence (MA-XRF) (Alfeld et al. 2011), macroscopic X-ray diffraction (MA-XRD) (De Nolf et al. 2011), macroscopic Fourier transform infrared

scanning in reflection mode (MA-rFTIR) (Legrand et al. 2014) and visible/near-infrared (Vis/NIR) imaging (Daffara et al. 2005). Camera-based analytical approaches include hyperspectral imaging in the visible range (Vis; 350–700 nm), the near-infrared range (NIR; 0.7–1.7 μm) and the short-wave infrared range (SWIR; 1.7–2.5 μm) (Delaney et al. 2014; Dooley et al. 2014).

To illustrate the interplay between spectroscopic methods for macroscopic, mobile and microscopic pigment identification and imaging, we offer an example of their combined use for a full characterization of the 15th century work of art *Christ with singing and music-making Angels*, by Hans Memling (1430–1495) (FIG. 1A). This painting was commissioned by Spanish merchants for the monastery of Santa Maria la Real de Nájera (Spain) and is currently under restoration.

MACROSCOPIC IMAGING AND MULTIPLE POINT ANALYSIS OF *CHRIST WITH SINGING AND MUSIC-MAKING ANGELS* BY HANS MEMLING

The panels of *Christ with singing and music-making Angels* (Royal Museum of Fine Arts, Antwerp) were extensively analyzed by means of portable and non-invasive FTIR, XRF and XRPD (Van der Snickt et al. 2011). The relatively short acquisition times for PXRF and PFTIR meant that they could be used as quick screening tools; on a more limited number of locations XRPD patterns were recorded using significantly longer measuring times. Together, these techniques could give a comprehensive overview of Memling's pigment usage. The following pigments were found to be present: lead tin yellow (type 1, Pb_2SnO_4), azurite [$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$], ultramarine ($\text{Na}_7\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_3$), lead white {hydrocerussite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$] and cerussite [$\text{Pb}(\text{CO}_3)$]}, a green organo-copper complex, brown and yellow earths (containing goethite [$\text{FeO}(\text{OH})$]), vermilion (HgS) and 'madder lake' (containing the red dyes purpurin and alizarin). Compared to the inorganic substances, the presence of the latter dyes (in areas coloured pink to burgundy) was more difficult to ascertain but was accomplished via reflection mode UV–Vis fluorimetry. A striking observation was the omnipresence of azurite as the blue pigment; only for the blue gems on Christ's cloak did Memling apply a thin glaze of costly ultramarine over the azurite. In all panels' ground layer both chalk and gypsum were found in various locations. The presence of gypsum was unexpected because this is a grounding material more closely associated with Southern European easel painting than with the 15th century Northern European painting tradition. The presence of quartz and goethite in the

gilded areas suggests the use of water gilding, involving the application of thin gold foil on a red clay substrate layer.

FIGURE 2 shows an area of the central panel where Memling succeeded in creating a wide scala of colours and optical effects: the wing of angel #8 is rendered in dark blue over blueish green to purple and red tones. The PXRF spectrum of blue area A revealed only Cu (as azurite) and Pb (as lead white) as the colour-determining elements; in the green-blue area B, it is a mixture of azurite and lead tin yellow that appears responsible for the colour. In the bright red area, HgS (vermilion red) is present, but visual inspection also revealed a transparent red overglaze layer (madder lake). The PXRF/PFTIR spectra of area C only indicates azurite: thus, a combination of madder lake and azurite appears to be responsible for the purple tone. Finally, in area D, a simple madder root glaze that covers a lead white modelling layer appears to have been used to obtain the reddish-pink tone.

The MA-XRF and MA-FTIR maps of FIGURE 3 provide more information on Memling's painting and colour rendering technique. The spectra were recorded using the devices shown in FIGURES 1C and 1D, respectively; they consists of a moveable XRF or FTIR measuring head mounted on a motorized X-Y stage (Alfeld et al. 2011; Legrand et al. 2011). The XRF head consists of an X-ray tube fitted with an X-ray polycapillary lens and an energy dispersive detector; the FTIR device employs curved mirrors, which focus the external IR beam into a millimetre-sized spot, a Michelson interferometer and a deuterated triglycine sulfate (DTGS) detector. Museum professionals, including art historians and painting conservators who are less familiar with spectroscopic techniques, find these XRF and FTIR maps easier to interpret than the large series of spectral data from many single points. The maps permit them to intuitively associate key chemical elements or compounds (and the corresponding pigments) with areas of a specific colour. In the case of *Christ with singing and music-making Angels*, the following six conclusions from the maps can be drawn:

- (1) Vermilion red (HgS) was used in the cloak embroidery and in the red parts of the wing of angel #8; it was used at a lower concentration level in the flesh tones of the face. Vermilion is very often intermixed with lead white, no matter what it is used for.
- (2) In the more purplish tones of angel #8's wing, madder lake is the major colorant, sometimes together with azurite.

(3) Azurite was employed in all blueish areas, but is contaminated with Zn.

(4) The hair of angel #8 was mostly painted using clay-containing earth pigments (Fe, e.g. from goethite), with lead tin yellow used in the light yellow highlights.

(5) Missing portions in the pictorial layer are evident from areas lacking XRF signals of Pb, Sn and Cu/Zn and FTIR signals of carbonate. These show an intense Ca signal and somewhat elevated Fe signals (from XRF) that originate from the ground layer and/or filling material and that coincide with elevated sulfate FTIR signals indicative of gypsum.

(6) The worn gilded background features high Au and reflected infrared signals but also Ca and Fe signals, both of which originate from an underlying adhesive bole layer.

In the indicated areas, almost no indications of *pentimenti* (intentional changes made by the painter) were encountered. This is not the case for other Memling panels where sometimes very substantial changes to the positioning of figures, or even the entire composition, could be revealed by means of chemical imaging.

PAINT CROSS SECTIONS ANALYSED BY MULTIMODAL X-RAY TECHNIQUES

Paint cross sections are conventionally embedded in resin and morphologically and compositionally characterized by SEM-EDX in combination with optical microscopy. The various layers are relatively easy to distinguish from each other by using secondary electron imaging (SEI) and/or backscatter electron imaging (BEI), with contrast and colour information delivered by visual and fluorescent light microphotography. FIGURE 5A shows an optical micrograph of a paint fragment (see FIG. 1D for the sampling position) in which one can see several layers containing coloured mineral grains of different type and size. FIGURES 5B and 5C show the corresponding SEI image and SEM-EDX element maps, which reflect the major compositions of the various layers. The distributions of S and Ca suggest that the ground consists of a central layer (layer 2, FIG. 5E) of chalk (CaCO_3) – a grounding material traditionally employed by Netherlandish painters of the 15th–16th centuries – but that two extra layers (layer 1 and layers 5–6) are present, both of which contain Ca and S: this suggests gypsum, which is a type of ground more typically associated with the Mediterranean region, including the Iberian Peninsula (Antunes et al. 2014; Rodriguez et al. 2010). In addition, two thin P-containing layers appear to be present:

the first one is directly on top of the preparation layer and contains black particles (see microphotograph), suggesting the use of bone black as underdrawing material. Note, however, that the second P-rich layer is actually an artefact that stems from spectral overlap with the Au-M emission line. Below the gold foil (see Au-L map as part of FIG. 5C) a preparatory Fe- and Pb-based adhesive bole layer is present. At the sampling spot, the purplish paint of the angel's clothing overlaps with the golden background so that the paint stratigraphy contains two additional strata that appear in the SEM-EDX maps as a single Pb-rich layer. One of these contains large bright-blue Cu-rich grains, suggesting the presence of azurite. In combination with red madder lake, the presence of azurite results in the purple colour of the angel's dress: the presence of madder itself can only be deduced indirectly from the distribution of potassium, part of the alum substrate on which the organic dye was precipitated. Even though the SEM-EDX data do not permit a detailed determination of which (inorganic) materials are present in each layer, the combination of element content, colour and contextual and historical knowledge allows us to infer a great deal about a given layer's (major) composition.

Though not directly visible in the maps of FIGURE 5C, two shortcomings of the SEM-EDX technique are (a) that the effective lateral resolution is mainly determined by the size of the interaction volume of the primary electron beam with the material, which here is on the order of several micrometers and this may be insufficient to sharply visualize the thinnest strata; (b) the information obtainable via SEM-EDX spectra or maps is limited to the major constituents. For example, distinguishing between two Cu-containing pigments, one polluted at the minor level (<1,000 ppm) with Zn while the other is not, is difficult to impossible. To make the analysis of these complex multilayered samples more material- and layer-specific, several complimentary methods must be employed. (confocal) Raman microscopy is one such method that can chemically distinguish between very thin paint layers, but requiring a judicious selection of the laser wavelength to avoid high fluorescence backgrounds and careful adjustment of the laser intensity to eliminate unwanted laser-induced chemical transformations.

FIGURES 5D and 5E summarise the results of a combined μ -XRF/XRPD scanning experiment over the area indicated in FIGURE 5A ($127 \times 90 \mu\text{m}^2$). This involved moving a highly monochromatic (21 keV) and intense (10^{11} photons per second) X-ray beam (generated in the PETRA-III synchrotron in Hamburg, Germany) of 0.4 μm diameter

in steps of 1 μm in the x- and y direction. At each beam position, X-ray fluorescence data were collected in reflection mode. Simultaneously, behind the sample, an X-ray sensitive camera records the diffraction pattern produced by the irradiated material (see FIG. 4 for a schematic of the apparatus set-up).

In FIGURE 5D, a composite of the resulting μ -XRF elemental maps is shown. This contains essentially the same information as the SEM-EDX maps of FIGURE 5C, except that the effective resolution is now defined by the step size of the scan. Along its path, the primary beam broadens only to a negligible extent as a result of scattering interactions. In the μ -XRF maps, the higher resolution also allow us to see a difference in texture between layers 1 and 5–6, the lower one composed of coarser gypsum grains than the upper one. Near the top of the paint stack one or more thin layers are visible (layer 7) of a Ca-containing material, that appear to have precipitated on the outer surface of the original (Pb-containing) layer. The unambiguous identification of most inorganic materials in the paint stratigraphy is possible by employing the information summarized in FIGURE 5E. The distinction between layers 1 [calcite, $\text{Ca}(\text{CO}_3)$] and 2 [gypsum, $\text{Ca}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$] is clear. In layer 3, hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$] can be identified, confirming the suspicion that one or more layers of bone-black are present. Immediately on top of these layers we find a thin layer of goethite [$\text{FeO}(\text{OH})$] (the bole layer). The XRPD maps confirm that the purplish paint layer covering the gold foil is twofold. The lower layer (layer 5) has a lead white matrix (mainly hydrocerussite in this case), with large blue-green grains of a non-crystalline, Cu-rich material. Although, based on PFTIR, azurite appears to be omnipresent, no XRPD signals of azurite were detected here. Surprisingly, in layer 6, Pb was not present as a carbonate but as PbSO_4 , the greyish mineral anglesite. As anglesite is not a painting material (Eastaugh et al. 2008), it is plausible that this is a degradation product formed from available Pb^{2+} -ions that were already present in the same layer and meeting (highly mobile) SO_4^{2-} ions that originated either from the gypsum ground layer or from an exterior source. To complete the complex stratigraphy, on top of the outermost (varnish) layer 7, the XRPD maps show a thin precipitation layer of weddellite [calcium oxalate, $\text{Ca}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$]. This compound possibly resulted from a natural degradation phenomenon: oxidative splitting of long aliphatic fatty-acid chains, which are present in the oil, gives rise to shorter, more oxidized, molecules such as oxalates. Oxalates of the metal ions Ca^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} have been encountered in many (degraded) works of art of the same or younger periods (Salvadó et al. 2009); PFTIR spectra and macroscopic maps (FIG. 3, left side)

from *Christ with singing and music-making Angels* revealed these compounds to be abundantly present here as well. The less-specific μ -XRF maps, which are generated simultaneously with the XRPD distributions, serve to link up with other microscopic data (e.g. the SEM-EDX maps) and are useful for pinpointing non-crystalline materials in the paint (such as the blue/green Cu-rich grains present in layer 5). In this case, most layers are flat and can be oriented relative to the primary beam such that the interface between the layers can be sharply imaged. In case of more complex paint morphologies, the related method of XRPD tomography (e.g. Vanmeert et al. 2015) can be employed. This method separates the XRPD contributions of various layers present in a paint stratigraphy from each other, leading to increased insights about the composition of each layer (De Nolf et al. 2010). The technique of confocal XRF can potentially do the same type of analysis (Janssens et al. 2010; Kanngiesser et al. 2012).

CONCLUSIONS

Examination of works of art by painters from various time periods such as Van Eyck, Goya, Rembrandt, Rubens, Van Gogh and others by means of constituent-specific macroscopic hyperspectral methods (e.g. MA-XRF, VNIR and/or MIR imaging) have demonstrated that these new tools are very useful for art historians and for art restorers alike, revealing information hitherto inaccessible. To complement the *in plane* information with *in depth* data, the use of highly-specific microscopic imaging methods such as combined μ -XRF/XRPD and/or based on vibrational spectroscopies is very appropriate. Thus, a far more complete overview can be constructed of the presence/usage of the various (crystalline) minerals or other pigments that were originally used to produce a painting. The new methodologies also allow us to see the *in situ* secondary products that often develop inside paint layers as they age and/or interact with their local environment.

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FIGURE CAPTIONS

FIGURE 1 (A) Fifteenth century painting *Christ with singing and music-making Angels* in three panels (inventory numbers 779, 778 and 780) by Hans Memling (1430–1495), held in the Royal Museum of Fine Arts, Antwerp (Belgium) and measuring 1.70 m x 6.70 m. The depicted angels are numbered 1 to 16. PHOTO BY RENÉ GERRITSEN. (B) Portable XRF (PXRF) analysis of the chest area of angel 8 in panel 778. (C) Macroscopic (MA-) XRF scanner analyzing part of angels 12 and 13 in panel 780. (D) MA-rFTIR scanner in front of angel 5 in panel 779. (E) Close-up of the heads of angels 6, 7 and 8 in panel 780; the green arrow indicates the original position of the paint micro-sample shown in FIGURE 5.

FIGURE 2 Detailed analysis of angel 8 in panel 778 (see Fig. 1). (LEFT) Relative X-ray fluorescence (XRF) signal intensity versus energy, showing characteristic peaks for Pb, Ca, Fe, Cu and Sn. The four spectral marked A, B, C, D correspond with areas marked on the upper-right figure. (UPPER RIGHT) Areas in the angel 8 painting subjected to analysis and identified by lettered boxes. The primary pigment(s) used in each zone are indicated by the colored boxes to the left and right of the image. (LOWER RIGHT) Fourier transform infrared (FTIR) spectra (intensity versus

wavenumber) for the analysed areas A, B, C and E of angel 8. Gy: Gypsum; Az: Azurite; LW: Lead White; Ox: oxalates.

FIGURE 3 Distribution maps from part of angel 8 in panel 778 (see Fig. 1) obtained using macroscopic X-ray fluorescence (MA-XRF) and macroscopic Fourier transform infrared spectroscopy in reflection mode (MA-rFTIR). The 8 large elemental maps are the MA-XRF distributions of Ca, Sn, Cu, Pb, Au, Zn, Fe and Hg. The yellow square indicates the location of the 8 smaller MA-rFTIR maps shown on the right.

FIGURE 4 Schematic of a synchrotron-based micro-X-ray fluorescence/X-ray powder diffraction (μ -XRF/ μ -XRPD) combined scanning experiment. The primary X-ray beam (21 keV, focused to $0.4 \times 0.4 \mu\text{m}^2$ diameter) scans the paint cross section and irradiates a cylinder of material from which XRF and XRD signals emerge. These are recorded in reflection and transmission mode, respectively, by the appropriate detectors.

FIGURE 5 (A) Optical micrograph of an embedded paint cross section, taken from the location of the arrow in FIGURE 1E (panel 780). (B) Secondary electron image of the paint cross section shown in (A). (C) Scanning electron microscope–energy dispersive X-ray spectroscopy (SEM-EDX) element maps, using selected elements' K and L spectral lines, of the cross section shown in (A): Ca(K), S(K), Pb(L), P(K), Au(L) and Cu(K). (D) Composite micro-X-ray fluorescence maps of cross section shown in (A) where red = Pb; green = Cu; blue = Au; yellow = Fe; white = Ca. (E) Micro- X-ray powder diffraction maps of cross section shown in (A) where magenta = weddellite; cyan = anglesite; red = the sum of hydrocerussite and cerussite; blue = gold; yellow = goethite; green = hydroxyapatite; orange = calcite; white = gypsum. Numbers 1 to 8 represent layers discernable in (E).