The examination of works of art using *in situ* XRF line and area scans

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Spatially resolved element distributions generated by *in situ* X-ray fluorescence (XRF) line and area scans are shown to provide information about works of art which may not be obtainable from single spot spectra. In addition to generating visually powerful element maps and line profiles, this method also generates a spectrum at each image point, and this large data set is available for additional analysis. When generating line and area scans in the study of works of art, the collection parameters – including X-ray tube choice, spot size, step size, and scan time – must be optimized not only to produce the best signal, but also to perform the analysis within constraints imposed to ensure the security or safety of the object. Examples of the application of this method to several classes of works of art are presented, including illuminated manuscripts, paintings, bronze sculpture, and glazed ceramics. Copyright © 2010 John Wiley & Sons, Ltd.

Introduction and Background

In the study of works of art or other precious materials, the ability to employ nondestructive analytical methods which can be used *in situ* is essential, as the removal of samples for analysis is generally severely limited, or in many cases forbidden. As such, X-ray fluorescence (XRF) has arguably become the most widely employed analytical technique in the scientific examination of works of art and other cultural heritage materials.^[1–9] Many configurations of XRF spectrometers are available,^[10,11] both commercially and as custom-built instruments; this paper will focus on the tube-based instruments with energy-dispersive detection most commonly employed in the examination of works of art.

Energy-dispersive XRF spectrometry had reached technological maturity by the early 1970s, but it was not until the 1980s that open-air architecture air-path instruments were developed specifically for the *in situ* examination of works of art.^[6,12,13] Employing either direct or secondary target excitation with a combination of collimators or filters to further condition the X-ray beam, these instruments produced excellent count rates with relatively high spatial resolution (on the order of <1 mm). However, although the open-air configuration allowed *in situ* examination, X-ray safety considerations restricted the operation of these instruments to within specially constructed lead-shielded rooms, thus limiting the works of art that could be analyzed to those that could safely be transported into the X-ray room. Furthermore, in order to ensure the safety of the artwork, these instruments were designed with a relatively long air-path (~2 cm), which resulted in attenuation of fluorescence from low-Z elements. Although some modifications could be made to evacuate or purge the X-ray path, in general only elements with $Z > 20$ could routinely and reliably be detected. In the 1990s, the first XRF spectrometers coupled to a scanning stage to generate spatially resolved XRF information were developed. Large flat-bed scanner type instruments^[14] were developed which could map large paintings. Benchtop instruments with sealable sample chambers provided the ability to carry out analyses under helium or in vacuum, thus facilitating the detection of low-Z elements.^[15] However, both types of instruments were limited in terms of the size and type of objects that could be examined.

With the development of handheld portable XRF spectrometers, the number and types of objects which can be analyzed has increased dramatically.^[16–20] Since these spectrometers can be taken directly to a work of art, immovable or otherwise inaccessible objects, such as monumental sculpture or architectural elements, which previously could only be examined by the removal of samples, can now be examined noninvasively *in situ*. However, with portability comes the loss of some functionality. The use of low power X-ray tubes allows the instrument to be used safely without external shielding, but the reduction in X-ray output necessitates the use of a larger beam aperture (on the order of several millimeters in diameter) to achieve desirable count rates. Although the excitation profile may be somewhat shapeable through the use of filters and control of the tube voltage and current, multiple instruments (with different anodes) may be necessary to provide optimal excitation profiles for all elements. The single spot analyses provided by these instruments are well suited for examining areas on objects that are homogeneous on the order of the size of the output aperture, such as is the case for most photographs,^[21–23] the bulk alloy of bronze sculpture,^[24,25] and ceramic bodies.^[26–28] However, many works of art, most notably illuminated manuscripts,^[29–32] drawings,^[31,33] and inlaid metals or painted enamels,^[34] have fine-scale features that cannot be adequately probed with these spectrometers. Furthermore, in many cases, it is the *distribution* of elements across a region that is of particular interest, which can be only roughly approximated using single spot analyses. For example, as will be discussed below, the use of elemental mapping can help identify an artist's characteristic palette and painting technique, or even reveal a hidden painting.

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In recent years, polycapillary optics^[35–45] have been used to create a new generation of XRF spectrometers with high spatial resolution – termed micro-XRF, μ -XRF, or MXRF. Coupling these micro-focus sources to motorized xyz stages provides the added ability to create line or area maps with sub-millimeter resolution. Polycapillary optics have been incorporated into benchtop instruments,^[15,46–48] but the size and type of works of art which can be examined by these instruments is extremely limited. Micro-XRF can also be carried out using a synchrotron source,^[5,49–53] but while synchrotron radiation offers many advantages in terms of control of the X-ray source and the ability to perform confocal imaging,^[54–56] the transportation of a work of art to the synchrotron source is a major undertaking, and would be impractical – and unnecessary – for the majority of analyses. For the examination of works of art and other cultural heritage materials, the ability to perform analyses in-house is critical where the safety and security of the object is of paramount importance.

This paper presents examples of line and area XRF scans acquired from works of art representing a range of media, including illuminated manuscripts, paintings, bronze sculpture, and glazed ceramics. The advantages and limitations of using line and area scans as opposed to individual spot analyses will be discussed in the specific context of the examination of works of art.

Experimental

An ARTAX 800 XRF spectrometer^[37] (Bruker AXS, Billerica MA, USA), was employed for all work presented here. The instrument was equipped with three interchangeable X-ray tubes with Cr-, Mo-, and W-targets. The Mo-target tube was fitted with a polycapillary lens, providing a nominal spot diameter of 65 μ m, while the Cr- and W-target tubes were each fitted with 650 μ m diameter collimators; for each tube, the collimator or polycapillary lens could be removed, producing a 2 mm diameter spot. Other X-ray tube and optics configurations are available from the manufacturer. The X-ray tubes could be operated at accelerating voltages between 12 and 50 kV with currents up to 1000 μ A; the operating parameters for each of the scans presented here are indicated in the corresponding figure captions. A motorized xyz stage was used to control the tube position, providing translation of up to 50 mm in each direction. The working height of the tube above the object is between 3 and 5 mm (depending on tube/collimator configuration); a digital camera and laser focusing system was used to determine the optimum position. Although not used in the examples discussed here, filters are available to condition the X-ray beam, and the object-detector path could be purged with helium through gas jets directed at the sample surface to enhance detection of low-Z elements.

XRF spectra were collected in one of three modes: spot analysis, line scan, or area scan. As with any scanning analysis, using the smallest available X-ray spot and step sizes together with long collection times typically produces the best results. However, when mapping large areas, this may result in unacceptably long scan times. For example, a 50 mm $\times$ 50 mm area map using the polycapillary lens (65 μ m diameter), stepping 0.6 mm between points, and collecting each spectrum for 30 s would take nearly 1 year to complete. This is obviously impractical. However, through careful selection of the collection parameters, including scan area, spot size, step size, and scan time, the information to be gathered can be optimized while respecting the limitations imposed to ensure the safety and security of the work of art.

As will be discussed with regard to the specific examples shown below, the micro-focus X-ray tube (Mo-target, 65 μ m diameter) was generally employed only when the particular feature of interest was on the order of 1–2 mm or smaller; the fine focus X-ray tube (650 μ m diameter spot, W-target) was employed for all other applications. The maximum step size was generally set to be on the order of the beam diameter. If time allowed, the spots were overlapped slightly using smaller step sizes, thus ensuring even coverage by compensating for intensity falloff near the edges of the beam.

Line and Area Scans of Works of Art

Manuscript illuminations

The term ‘miniature,’ used to denote a picture in a manuscript, originates from the classical Latin term *minium* for the red pigment commonly used in manuscripts.^[57] However, since paintings in manuscripts typically are executed on a very small scale, the modern definition of the term ‘miniature’ is also fitting. Often, the finely executed details found in many of these works of art can only be seen with the aid of magnification. As such, manuscript illuminations and illustrations are particularly well suited for examination by micro-XRF line and area scanning.

An example of the use of micro-XRF area and line mapping to study a finely painted detail within the manuscript miniature *Bathsheba Bathing* (Jean Bourdichon, Hours of Louis XII, 1498–1499, JPMG Ms. 79/2003.105) is presented in Figs 1–3. A detail of the miniature is shown in Fig. 1(a). The tree behind Bathsheba [outlined in Fig. 1(a) and shown in Fig. 1(b)] is covered with yellow apples that are less than 2 mm in diameter. Under magnification [see inset in Fig. 1(b)] these apples can be seen to be composed of three distinct components: the yellow body of the apple, red shading along the bottom and right edges, and a tiny white highlight in the center. An XRF area scan was collected over this apple, covering an area of 1.61 mm $\times$ 1.68 mm, using the Mo-target X-ray tube fitted with the polycapillary lens (65 μ m diameter spot) and a step size of 70 μ m; the resulting element maps are presented in Fig. 2. Even with the relatively short collection time of 20 s/spectrum, it required approximately 5 h to complete the scan, but resulted in quite detailed maps of the various pigments used to paint the apple.

The distribution of mercury [Hg $L\alpha$ line, shown in Fig. 2(a)], corresponds to the red shading along the edge of the apple, suggesting the red pigment vermilion (HgS, mercuric sulfide) was used to paint this feature. The elements lead [Pb $L\alpha$ line, Fig. 2(b)] and tin [Sn $L\alpha$ line, Fig. 2(c)] cover the entire area of the apple and show strong correlation with each other, suggesting the use of a lead–tin yellow pigment (either type I, Pb_2SnO_4 ; or type II, $PbSn_{1-x}Si_xO_3$). The Pb $L\alpha$ and Sn $L\alpha$ maps reveal another interesting feature: the area corresponding to the white highlight in the center of the apple (near coordinate position $x = 0.8$ mm, $y = 0.8$ mm) shows increased Pb and decreased Sn with respect to the surrounding areas, suggesting the use of the pigment lead white [basic lead carbonate, $PbCO_3 \cdot Pb(OH)_2$] to paint this feature. It should be noted that the apparent decrease in Sn content in this area is an artifact resulting from the fact that in this area the lead–tin yellow is covered by a layer of lead white, which attenuates the Sn XRF emission. The area surrounding the apple was found to contain primarily copper [Cu $K\alpha$ line, Fig. 2(d)], with small patches of tin and lead also present, suggesting the use of the green pigment

Figure 1. (a) Detail from Jean Bourdichon, *Bathsheba Bathing*, Hours of Louis XII, 1498–1499 [JPGM MS 79 (2003.105)] and (b) detail of tree behind Bathsheba and photomicrograph of apple on which XRF mapping was performed.

Figure 2. XRF area maps of apple shown in Fig. 1, showing net integrated area under the (a) Hg $L\alpha$ (intensity plotted on log scale for clarity), (b) Pb $L\alpha$, (c) Sn $L\alpha$, and (d) Cu $K\alpha$ lines. Collection area 1.61 mm × 1.68 mm, 0.07 mm/step, 20 s/spot, Mo-target X-ray tube, polycapillary lens (65 μm diameter) operated at 40 kV, 600 μA.

malachite ($\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) and/or the blue pigment azurite ($2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$) mixed with lead–tin yellow. The presence of vermilion, lead white, lead–tin yellow type I, azurite, and malachite was confirmed by Raman microspectroscopy.^[29]

As mentioned briefly above, along with providing a measure of the distribution of individual elements, XRF data can also provide information about the order in which the pigments were applied

by taking into account the re-absorption of fluorescent X-rays by layers of high-Z pigments. The relative position of the pigments within the apple can thus be determined from an examination of the area maps shown in Fig. 2: the vermilion highlight was painted over the lead–tin yellow apple, which in turn was painted on top of the copper-based green background. This same information can be represented on a single graph, shown in Fig. 3, by extracting

Figure 3. XRF line scans extracted from y-position 0.77 mm (indicated by dotted line) from the four area maps presented in Fig. 2; the curves have been offset for clarity.

a line of data across the center of the apple. In this graph, moving across the apple from right to left, the concentration of Hg has a peak between 0.07 and 0.35 mm, corresponding to the stroke of red paint visible on the surface. The yellow body of the apple, between positions 0.35 and ~0.65 mm, and again between positions 1.12 and ~1.45 mm, contains similarly elevated levels Pb and Sn, consistent with its identification as the pigment lead–tin yellow. The white highlight in the center, between positions ~0.65 and ~0.95 mm, shows a further increase in Pb content relative to the adjacent lead–tin yellow areas, and an apparent decrease in Sn, which, as discussed above is an artifact due to absorption by the overlying lead white layer. Although Cu is present under the entire apple (based on visual examination and traditional painting techniques), its fluorescence signal is suppressed in those areas covered by Pb-containing pigments. This is confirmed by the apparent spike in the Cu content between positions ~0.95 and 1.12 mm, corresponding to an area where the lead–tin yellow pigment layer is discontinuous.

Elemental information alone, while providing an indication of the pigments which may be present, is insufficient for definitive pigment identification. Raman microscopy can provide molecularly specific identification of individual pigment particles, but this strength is in some ways also its weakness: it does not provide information about relative amounts or distributions. Raman mapping is possible,^[58] generating maps with down to sub-micron resolution, but it is considerably more sensitive to variation in the z-direction than XRF mapping and thus, in general, is most appropriate for generating maps of very small areas (on the order of 1 mm²) on microscopically flat surfaces. Therefore, XRF mapping is more appropriate for examining painted features of the size and shape typical of those found on manuscript miniatures. In addition, XRF mapping offers the advantage in that all elements are probed simultaneously, whereas multiple Raman maps may

need to be acquired using different excitation wavelengths to effectively excite the various components of a mixture.

This example demonstrates how XRF area and line scans can provide detailed information regarding finely painted features in manuscript illuminations that would not be accessible through single spot XRF analyses or other *in situ* scanning methods. The high-resolution area scans of the apple not only generated visually compelling element distribution maps, but by extracting a line scan through points of interest the relative position of each element within the paint structure could be elucidated through consideration of absorption effects. Not all features in manuscript miniatures may require scanning at the highest resolution, and features with a high degree of symmetry may only require scanning across one dimension – a line scan – in order to obtain the required information. In the examination of works of art, before conducting any instrumental analysis, it is always recommended to carry out a careful microscopic visual examination, especially at cracks and edges, in order to get an idea of the possible layer structure. This information, coupled with XRF and Raman data often enables the researcher to generate a complete picture of the pigments used, and in what order they were applied, through completely noninvasive analysis.

Paintings

Prior to the 15th century, paintings were executed in tempera, in which thin layers of pigment suspended in an egg-based medium were applied to prepared wooden panel supports.^[59,60] By contrast, oil paint, which was widely adopted in Europe by the end of the 15th century, allowed artists considerably more freedom with respect to mixing colors, melding layers, and correcting or even reworking a painting. In the study of paintings, and oil paintings, in particular, the composition and stratigraphy of the paint layers can provide insight into the working practices of the artist.^[61] Typically, this information is obtained by the removal of small (< 1 mm³) samples, which are mounted in polyester resin and either polished or sectioned using a microtome to reveal a cross section of the painting's structure in a particular area.^[62] However, sampling is usually limited to the edges, or damaged areas, of a painting and as such cannot provide an accurate picture of the overall underlying structure. Due to the penetrating characteristics of X-rays, XRF spectroscopy provides a noninvasive means by which information about subsurface paint layers can be obtained.^[63,64] For example, the relative intensity of the Pb L-emission lines changes in a predictable way depending on the depth of the Pb-containing pigment and composition of overlying layers.^[7] While information about the relative position of elements within a layered structure may be extracted from individual spot spectra, elemental mapping provides the ability to determine the painted form, as well as the elemental composition, of the underlying layer.

A hidden painting is known to lie underneath Rembrandt's *Old Man in Military Costume* (Rembrandt van Rijn, 1630/1631 AD, JPM 78.PB.246),^[65] shown in Fig. 4(a)). The location and general shape of the hidden painting – a portrait – was initially revealed by X-radiography and autoradiography. The hidden portrait, which can be seen in the X-radiograph shown in Fig. 4(b), is inverted with respect to the portrait on the surface, and fortunately, the two faces do not overlap. The attribution of paintings to Rembrandt is complicated by the fact that he shared a workshop with students and followers. Having the material composition and form of the hidden portrait to compare with the surface portrait of the *Old*

Figure 4. (a) Rembrandt Hardens van Rijn, *Portrait of Old Man in Military Costume*, 1630/1633 (oil on panel, JPGM 78.PB.246) and (b) X-radiograph of painting, inverted to show underlying portrait; inset contains XRF area map (generated from net integrated area of Hg L α line) in region of lips of underlying portrait. Collection area 30 mm $\times$ 20 mm, 1 mm/step, 30 s/spot, W-target X-ray tube, (650 μ m diameter collimator) operated at 40 kV, 600 μ A.

Man, and other well-attributed Rembrandt portraits, may assist art historians in determining the attribution of the hidden portrait. XRF spot analysis identified mercury in the region of the hidden face, suggesting the presence of the pigment vermilion. However, it was not until an area scan of the region [inset in Fig. 4(b)] was collected that it became clear that the vermilion corresponded to the shape of the lips of the figure in the hidden portrait. Several areas on the painting were similarly tested, to gain a better understanding of the elements contained in the hidden portrait, and to begin to understand their distribution.

Mapping elements in a hidden painting using XRF has been carried out successfully using synchrotron radiation sources.^[51,56] However, as demonstrated here, preliminary work using spot and/or area mapping is helpful for determining the location and possible identity of pigments of interest and evaluate whether or not the information to be gleaned from synchrotron experiments justify the extra risk to the painting associated with transporting it to a synchrotron source.^[66] Studies conducted in-house using a lab-based XRF spectrometer might therefore not only serve in the planning of synchrotron experiments, but in some cases may be sufficient to image the desired parts of hidden paintings.

Sculptures

XRF is particularly well suited to the study of bronze sculpture or other metal objects, since these works of art tend to be large, with smooth and relatively homogeneous surfaces, characteristics which also create one of the few opportunities in the study of works of art to perform quantitative XRF analysis.^[67–70] Determining the composition of the metal alloy, as well as the nature of any applied surface treatments,^[71] or join and repair materials, may

provide insight into the materials and practices characteristic of an individual artist, or the foundry technology of a particular era.^[24,25] For sculpture, the composition of repairs and solder joins is a means of determining whether or not the object has undergone modification or repair subsequent to its original manufacture. These joins may be on the order of a millimeter or less in width, and an XRF spectrometer with an output aperture on the order of a few millimeters may not be able to adequately determine their composition, as the spectrum would be dominated by the surrounding metal. While it is sometimes possible to perform a spectral subtraction from an adjacent area, if the join is extremely thin or close in composition to the bulk alloy, there may be insufficient difference in the spectra to distinguish the two materials. In these cases, the high spatial resolution provided by a micro-XRF spectrometer would better probe the composition of extremely fine solder joins, or other similarly small features on a metal sculpture.

An example of the benefits of high-resolution elemental line scanning is provided in preliminary investigations of very fine joins and repairs on the 18th century Italian sculpture *Dancing Faun* [Fig. 5(a), Pietro Cipriani, 1722/1724 AD, JPGM 2008.41.2]. Employing the Mo-target micro-focus X-ray tube with the polycapillary lens, the spot size of $\sim 65 \mu$ m allowed the collection of a series of spectra every 30 μ m in a line across the join [black line in Fig. 5(b) indicates path of line scan across circular repair join], with multiple measurements made entirely within the join itself. The resulting element line profiles, shown in Fig. 5(c), revealed small, but definitive, increases in the amounts of tin, lead, and arsenic within the join. The presence of tin and lead confirmed this to be a solder join (as opposed to a brazed or glue-based repair). The detection of arsenic in the solder was

Figure 5. (a) Pietro Cipriani, *Dancing Faun*, 1722/1724 (JPGM 2008.41.2), dotted circle indicates region containing investigated repair, (b) surface detail of repair, black line indicates path of line scan, and (c) net integrated areas of Pb $L\alpha$, Sn $K\alpha$, and As $K\alpha$ lines. The Pb $L\alpha$ curve has been offset for clarity. Collection length 4.68 mm, 0.03 mm/step, 30 s/spot, Mo-target X-ray tube, polycapillary lens (65 μm diameter collimator) operated at 50 kV, 200 μA .

particularly interesting, as arsenic was also found in the alloy, as measured by spot analyses carried out at numerous locations across the entire sculpture. By providing information about the join material together with its relationship to the adjacent base alloy, element line scans can provide a more reliable means for the evaluation of joins than would have been possible from single spot analyses.

Glazed ceramics

In the study of glazed ceramics, the composition and thickness of the glaze material is usually a primary area of investigation, as this information may be used to determine the general region of origin, or perhaps even allow attribution to a particular workshop. For archaeological ceramics, in particular, evidence of diffusion of elements across the ceramic body–glaze interface may have implications for assessing the technology by which the piece was created.^[72] This work typically is performed on small removed samples mounted and polished as cross sections and analyzed using either scanning electron microscopy (SEM) or electron-probe microanalysis (EPMA), and the results reported in terms of standard oxide compositions.^[73] For the purposes of this study it was of interest to explore to what extent information obtained using micro-XRF line or area scans could inform or otherwise supplement these more traditional studies.

A sample of a second millennium BCE Mediterranean glazed ceramic [shown in Fig. 6(a)] was examined using the Mo-target X-ray tube with the polycapillary lens ($\sim 65\ \mu\text{m}$ diameter spot size); a rough line scan taken across the ceramic–glaze interface with spectra collected every 100 μm is shown in Fig. 6(b). This preliminary scan was completed in less than 15 min, but the results nevertheless clearly show the glaze layer (with a thickness of approximately 0.5 mm) to be rich in copper and the ceramic body to be rich in iron and calcium. Closer examination of the element

distribution profiles reveals that iron and calcium are present in the glaze layer as well, with decreasing concentration approaching the glaze surface. Such profiles typically indicate elemental diffusion from the ceramic body into the glaze layer. Subsequent electron microprobe analysis (not shown) collected across the interface similarly recorded the diffusion of these elements into the glaze layer.

This example serves to demonstrate the utility of XRF line scans to perform preliminary analyses quickly, and with little or no sample preparation. Although this example was performed on a prepared cross section, it might just as easily have been done *in situ* on a broken edge, thus serving as an effective preliminary study to help identify those areas from which samples should be taken for more in-depth study by one of the microscopic elemental analytical techniques mentioned above. Alternatively, XRF line and/or area scans might provide sufficient elemental distribution information to answer many technical art history questions, proving particularly beneficial for institutions without access to SEM/EPMA.

Conclusions

The case studies presented here were selected to illustrate the utility of *in situ* XRF line and area scanning in the study of works of art and highlight how the generation of spatially resolved elemental information often can provide important information not obtainable through single spot analyses. Area scans are best employed for questions regarding the distribution of elements throughout a complex, or unsymmetrical feature. However, if the feature changes along only one dimension, a line scan may be sufficient. In both cases, when examining works of art, the choice of operating conditions – spot size, step size, and scan time – must be optimized to achieve the desired information under the conditions

Figure 6. (a) Visible light photomicrograph of polished cross section from second millennium BCE glazed ceramic. Dotted line shows path of XRF line scan. (b) XRF line scan showing net integrated area of Fe $K\alpha$, Ca $K\alpha$, and Cu $K\alpha$ X-ray emission lines. Collection length 2.1 mm, 0.1 mm/step, 30 s/spot, Mo-target X-ray tube, polycapillary lens (65 μ m diameter collimator) operated at 40 kV, 600 μ A.

and time allowed. Initial scans using large spot or step sizes may be useful to determine those areas to be subjected to longer, more detailed scans; in some cases these quick scans may be sufficient to determine the information required.

Along with generating informative elemental distribution maps, line or area scans also have the advantage of generating individual XRF spectra at each point. Additional information may be gleaned from these spectra, such as the relative position of layers through the analysis of line scans and absorption effects on peak intensities, or the relative contribution of low-Z elements in the matrix through analysis of the Compton and Rayleigh scatter peaks.^[16] While spot analyses will undoubtedly continue to constitute the bulk of analyses performed on works of art and other cultural heritage materials, where possible and appropriate, the use of line or area scans should be considered.

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