INVITED PAPER

Development of a versatile XRF scanner for the elemental imaging of paintworks

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Abstract Scanning XRF is a powerful elemental imaging technique introduced at the synchrotron that has recently been transposed to laboratory. The growing interest in this technique stems from its ability to collect images reflecting pigment distribution within large areas on artworks by means of their elemental signature. In that sense, scanning XRF appears highly complementary to standard imaging techniques (Visible, UV, IR photography and X-ray radiography). The versatile XRF scanner presented here has been designed and built at the C2RMF in response to specific constraints: transportability, cost-effectiveness and ability to scan large areas within a single working day. The instrument is based on a standard X-ray generator with sub-millimetre collimated beam and a SDD-based spectrometer to collected X-ray spectra. The instrument head is scanned in front of the painting by means of motorised movements to cover an area up to 300×300 mm^2 with a resolution of 0.5 mm (600×600 pixels). The 15-kg head is mounted on a stable photo stand for rapid positioning on paintworks and maintains a free side-access for safety; it can also be attached to a lighter tripod for field measurements. Alignment is achieved with a laser pointer and a micro-camera. With a scanning speed of 5 mm/s and 0.1 s/point, elemental maps are collected in 10 h, i.e. a working day. The X-ray spectra of all pixels are rapidly processed using an open source program to derive elemental maps. To illustrate the capabilities of this instrument, this contribution presents the results obtained on the *Belle Ferronnière* painted by Leonardo da Vinci (1452–1519) and conserved in the *Musée du Louvre*, prior to its restoration at the C2RMF.

1 Introduction

X-ray fluorescence [1, 2] (XRF) is an efficient, fast, safe and firmly established method for the single spot measurement of elements present in paintworks [3–5]. The generalisation of this technique to a series of points covering a large area, initially developed with Synchrotron XRF [6], has been transposed to the laboratory in the form of scanning macro XRF (labelled MA-XRF), an imaging technique increasingly used for the investigation of painted artworks [7]. MA-XRF provides elemental maps that can be compared with great benefit to pictures recorded with different scientific imaging techniques [8, 9] using either X-rays with radiography [10], laminography [11], emissiography [12], or neutrons with the neutron autoradiography [13], or eventually photons in the ultraviolet to infrared domains [14] such as UV fluorescence, false colour infrared, IR reflectography, etc. Because of the high mass attenuation coefficient of lead, contrast in X-ray radiography is mainly reflecting lead white distribution, often present in the ground and the pictorial layers. As a consequence, the slight contrast induced in radiographs by lighter elements present in other pigments, e.g. copper, iron or manganese, is often obscured. In addition, when the preparation or the support is more absorbing than the paint layers (e.g. thick lead-white ground or wood panel support), X-ray radiography provides a poor image of the

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composition. Contrary to images obtained with X-rays in transmission mode, elemental images acquired in emission mode using MA-XRF are less affected by these considerations and appear highly complementary to X-ray radiography. The ability of MA-XRF to image pigment distribution by means of their elemental signature may qualify it, in some sense, as 'colour radiography'. Such optimistic considerations must, however, be moderated, as MA-XRF presents important limitations. Firstly, the low XRF cross section of light elements and the absorption of X-rays by the varnish layer and the air between the painting and the detector generally prevent imaging of elements with energy lines below 2 keV (sulphur). Secondly, acquisition of maps with fine resolution can be very time-consuming, often requiring days of operation. The acquisition of a satisfactory spectrum during the short time spent on each pixel (fraction of a second) requires the use of intense incident X-ray beams combined with high efficiency detectors able to stand large count rates. Finally, MA-XRF maps resolution is limited by the size of the X-ray beam. X-ray optics can be used to obtain small beams, but maintaining the painting in focus of the system can be difficult if its surface is not flat. Commercially available XRF scanners for paintworks overcome these limitations [15], at the expense of complexity, weight and cost (multiple detectors, focusing X-ray optics).

The versatile XRF scanner presented here was designed and built at the C2RMF in response to specific constrains: transportability, cost-effectiveness and ability to scan significantly large areas within a single working day. Indeed, MA-XRF imaging of paintworks often on display in a museum can only been carried out during closing days, preferably within working hours to ensure artefact safety. Concerning map size and resolution, our experience is that valuable results can be achieved by scanning paintings on areas of more than ten centimetres with a sub-millimetre step. The prototype of the MA-XRF scanner detailed here was first applied the study of Giotto's Cross from the Louvre museum and the results published elsewhere [16]. The present contribution details the specifications and performances of the MA-XRF instrument and illustrates its application to the *Belle Ferronnière* by Leonardo da Vinci (1452–1519) conserved at the Musée du Louvre, INV. 778, prior to its restoration at the C2RMF.

2 Materials and methods

The MA-XRF instrument is based on a standard X-ray generator also implemented in the ARTAX [17] spectrometer (BRUKER X1 generator, Mo tube model RTW MCB 50-0.6, 50 kV, 0.6 mA max). Emitted X-rays are collimated using a molybdenum pinhole (0.65 mm or

1 mm diameter) producing a quasi parallel beam (no X-ray optics) forming a spot size independent of the distance, thus unaffected from a possible non-flatness of the paintwork. XRF spectra are collected with a fast X-ray spectrometer (Amptek model X123 integrating a 25-mm^2 Fast SDD$^®$ detector). When operated in the laboratory environment, the 15-kg scanner head is mounted on a sturdy photo studio stand (FOBA DSS-ALPHA) allowing an accurate and quick positioning and permitting a free side-access to the artwork for safety (Fig. 1). For field measurements, the head can be mounted on lighter tripod (MANFROTTO). The X/Y/Z movements are achieved with stepping motor translations (OWIS LTM80 and PS35 controller) and a manual positioning pad. Precise alignment is obtained by visualising the spot of the laser pointer integrated in the X-ray tube on the painting surface with a micro-video camera (Toshiba QP49H, 8 mm objective). The scanned area extends up to 300×300 mm with a maximum resolution of 0.5 mm (600×600 pixels) set by the size of the X-ray collimator. With a scanning speed of 5 mm/s and a dwell time of 0.1 s, elemental maps at max size are collected in 10 h.

Fig. 1 MA-XRF instrument in front of the *Belle Ferronnière by Leonardo da Vinci (1452–1519), Musée du Louvre, INV. 778*

The MA-XRF instrument is controlled by a dedicated program implemented in a portable computer running under Windows®. The interface was built in Visual Studio and uses DLL libraries supplied by the spectrometer and translation stage manufacturers. The program controls the mechanical scan by an USB connection to the translation controller and simultaneously collects spectra by another USB connection to the spectrometer. Scanning is achieved at constant speed, and spectra are collected on the flight, on the basis of an internal system clock. Fluctuations of the acquisition real time per pixel are due to uncontrolled delays in the spectrometer and overheads in Windows which is not a real-time OS. To correct for these fluctuations, spectra are normalised to a common live time just after transfer.

Data (one spectrum per pixel) are stored in EDF format, one line per file, to be processed with the open source program PyMCA [18] developed for X-ray fluorescence at the European Synchrotron Research Facility (ESRF). Elemental maps in PNG format are derived with the Dataimaging program [19] developed at the C2RMF. The MA-XRF scanner program can be freely downloaded [20] and the required software libraries for the translations stages and the spectrometer obtained from the manufacturers.

This instrument has reached the limit permitted by its simple design. Indeed, the X-ray generator employed cannot produce a higher flux to allow to scan more rapidly or to increase statistics in the collected spectra. Collimating the X-ray beam to a smaller size would reduce its intensity, thus implying too long acquisitions because of the increased number of points. Extending to larger scan sizes (e.g. $500 \times 500 \text{ mm}^2$) with the same resolution requires heavier motorised translations, thus a loss of mobility and also longer scans. As concerns the detector, little progress can be expected. The 25 mm^2 SDD placed at minimum distance could be replaced by a bigger one, but the larger housing will procure a limited gain in solid angle. The number of points scanned per second cannot be increased either as the reading of spectra through USB is unreliable when using dwell times shorter than 0.1 s.

3 Application to the *Belle Ferronnière* by Leonardo da Vinci

3.1 Experimental

The MA-XRF scanner was applied to the so-called *Belle Ferronnière* painted by Leonardo da Vinci (1452–1519) on a walnut panel which is conserved at the Louvre museum (Fig. 2a). This investigation took place in the context of a restoration project of the masterpiece, in addition to a broader scientific study [21]. Two specific questions were raised by curators and conservators, namely the understanding of the dark background surrounding the women and the determination of the altered state of the worn area on the jaw of the figure.

The painting was first studied by X-ray radiography at 45 kV. This unusually high voltage was required to obtain a satisfactory image trough the lead-containing paint layers, the lead white and red lead ground layer, and the wood support. As can be observed in the radiograph (Fig. 2b), the ground produces horizontal and opaque strokes that are characteristic of a lead-based pigment priming. Secondly, the fact that the wood vessels remain visible as white images, on different radiographies conducted at increasing voltages (from 20 to 45 kV), indicates that a layer of lead-based pigment, and not a gesso (calcium sulphate), was directly laid on the wood. In addition, the cloudy and blurred images suggest that the lead-white ground was applied in form of a quite fluid material.

Due to the relatively large size of the painting (635×445 mm) and its mounting on an auxiliary wood support holding the original panel at the four corners for the restoration, it could not be scanned in a single pass. The MA-XRF was thus carried out in six scans, four large scans and two smaller ones. The X-ray generator was set at 40 kV and 1 mA, corresponding to the maximum power. Higher voltages would only enhance the predominant Pb L lines without relative gain for lines below 10 keV. Excitation of X-ray lines above Pb L lines (e.g. Ba-K, Sn-K, Sb-K) is not useful since these lines are poorly recorded by the SDD detector due to its efficiency drop-off above 15 keV. The L lines of the corresponding elements (Ba-L, Sb-L, Sn-L) are recorded with higher statistics. No beam filtering was used in order to benefit from the excitation at low energy with the X-ray continuum. The X-ray detector was placed at 15 mm from the painting. The four large scans of 165×200 mm were carried out with 0.5 mm steps using a 0.65 mm collimator. The acquisition time per pixel (dwell time) was fixed at 0.2 s, requiring 7 h 45 min for each 330×400 pixels scan. The total counts in each scan were about 3×10^8, 10^4 counts/s on average, each 512 channel spectra containing around 2200 counts. Because of the air path and the presence of a thick varnish layer (around 50 µm) absorbing low energy X-rays, the lightest measurable element was calcium and Pb-M lines were the lowest detected X-ray lines. Each dataset was processed with PYMCA to provide the full fitting of all spectra collected in scan, generating artefact-free elemental maps in 10 min on the portable computer.

4 Results

The dark background surrounding the woman mainly contains lead, copper, iron, and calcium. The iron and copper maps, however, look very different. The iron map

◄**Fig. 2** Images of the *Belle Ferronnière* prior to its restoration. **a** Direct light photograph © E. Lambert, C2RMF. **b** X-ray radiograph © E. Ravaud, C2RMF. **c** Infrared false colour photograph © E. Lambert, C2RMF. Note the unusual appearance and colour of the figure's jaw corresponding to a worn area which is indicated by the arrow

(Fig. 3a) shows a very even and smooth appearance without visible brushstroke. Its correlation with the calcium map (Fig. 3b), although noisy because of the above-mentioned absorption, suggests that iron is present in form of earth. On the other hand, the copper map (Fig. 3c) reveals important variations, with broad and irregular brushstrokes applied everywhere in the background. The borders of the figure are sharply delimited and underlined by stiff and heavy strokes containing copper that in some places simplify the contours (e.g. figure's neck and braid). Inside the figure, copper only appears in the ribbons of the dress. The marked discordance of the aspect of the iron and copper maps and their non-precise overlapping contours allow us to conclude that iron and copper are not linked. Two distinct layers, a first one containing iron and another one with copper, were applied in two times to form the background. A micro-sample taken from the upper right corner of the dark background confirmed the presence of the two layers. The SEM-EDX analyses indicated that the first one contains earth and carbon black and the second one a copper-based pigment, probably verdigris. The MA-XRF clearly shows here its ability to evidence distinct paint layers in a non-destructive way. Moreover, the careful examination of the maps recorded in the dark background permits to exclude the presence of any additional composition, pattern or shading that could have been missed in previous investigations.

The MA-XRF scan of the jaw also provides interesting information on this altered area. Previous investigations established that Leonardo painted the flesh tones of the *Belle Ferronnière* in two main steps [21]. The first consisted in a warm modulation of tones going from light pink to dark red, mainly achieved using haematite, as identified by X-ray diffraction. The second modelling was obtained by a cold white-to-black modulation using a glaze containing carbon black and lead white. This layer looks extremely thin (estimated to a few microns), in order to let the underlying warm layer shine through. Microscope examinations of the worn area on the jaw reveal that the alteration affects at least the cold glaze layer, probably as a consequence of a previous inappropriate cleaning. The question was to determine whether the damage was extending deeper in the paint layers. Whereas the visible light (Fig. 2a) and infrared false colour photographs (Fig. 2c) showed an abnormal red tone in this area, the MA-XRF iron map in reverse grey

and logarithm scale (Fig. 3d) reveals the extraordinary subtle gradient of haematite that forms the volume of the jaw. The jaw modelling thus appears intact on the iron map and it can be concluded that the warm under layer is preserved; only the very thin cold glaze is irregularly missing. The high quality of the images recorded with the MA-XRF instrument played a key role in their interpretation. The reported results reinforced the decision to undertake a very subtle retouching of the jaw in order to spatially reintegrate the worn area in the *Belle Ferronnière's* face.

5 Assessment of damage risks due to X-rays

Since the X-ray beam of this instrument is directed to a painting during hours, an assessment of the potential risks induced by this irradiation is necessary. One may compare the irradiation induced in a painting during an MA-XRF scan to that induced by X-ray radiography. In radiography, a painting is typically X-rayed at 40 kV, 5 mA during 3 min, with the X-ray tube placed at 200 cm distance. The corresponding conditions for a MA-XRF scanning are 40 kV, 1 mA, 0.1 s per point, 7 cm distance between the tube anode and the paint surface. Due to the difference in distances and intensities, the flux (X-rays/cm^2/s) in MA-XRF is 160 times more than in radiography, but the irradiation time is 1800 times shorter. The integrated radiation dose received by the painting during a MA-XRF scan (X-ray fluence in X-rays/cm^2), which is the relevant physical quantity in terms of potential damage, appears inferior (1/10th) to the dose used in a single X-ray radiography. The MA-XRF scanning technique can thus be qualified as safeas radiography.

6 Conclusions

The presented MA-XRF scanner appears as a useful tool for the study of paintworks. It allows the recording of elemental maps up to 300×300 mm^2 with a sub-millimetre resolution in a relatively short time. It almost reaches the maximum performance in terms of map size and resolution that can be achieved with a simple design based upon a standard X-ray generator and a single X-ray detector. Designed for conservation science laboratories, this instrument fulfils the objective of transportability, cost-effectiveness and ability to scan large areas within a single working day. Its first applications clearly demonstrate that despite lower performances compared to 2D XRF scanning carried out at the synchrotron or with high-end dedicated laboratory instruments, it provides useful results for a routine use in a museum environment.

◄ **Fig. 3** Elemental maps recorded on the *Belle Ferronnière*. **a** Iron map. **b** Calcium map. **c** Copper map. **d** Iron map in reverse and log scale. All maps © C2RMF

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