

# Imaging study of Raffaello's “La Muta” by a portable XRF spectrometer<sup>☆</sup>

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## ABSTRACT

In studies of Cultural Heritage, there is a growing demand for methods of material investigation. X-Ray Fluorescence (XRF) analyses have proven to be essential tools in these material studies. The XRF scanning spectrometer, developed at the LABEC laboratory in Florence, can perform both elemental mapping, on areas up to  $20 \times 20 \text{ cm}^2$ , and single spot analyses.

Thanks to our close and long lasting collaboration with the Opificio delle Pietre Dure in Florence, one of the most prestigious restoration centers in the world, we had the opportunity to use the new XRF spectrometer in analyzing the painting “La Muta” of Raffaello Sanzio, one of the “Old Masters” of the Italian Renaissance.

Beyond identification of the painting palette, the XRF study further allowed for structural analysis in cases where single spot XRF measurements would not be adequate. For example, the new system allowed us to deduce Raffaello's use of bone black pigment and to analyze various instances of “pentimenti” (underlying image in a painting, evidence of revision by the artist).

## 1. Introduction

As is well known, in Cultural Heritage (CH) studies there is a growing demand for methods of material investigation. Indeed, a deep knowledge of artworks can be crucial for a suitable conservation [1–3]. In particular, X-Ray Fluorescence (XRF) techniques [4,5] provide valuable insight regarding the material composition of artworks, as they allow for multi-elemental, non-invasive, and non-destructive in-situ analyses [6–10]. The scanning XRF spectrometer, recently developed at the LABEC laboratory of INFN (National Institute of Nuclear Science) in Florence in collaboration with the INFN network of laboratories for Cultural Heritage studies (CHNet), has proven to be of great help for

applications on paintings. Improving on previous, fixed-head designs, the new system allows for acquisition of elemental maps over a scanned area. Objects under study, even when exhibiting apparently uniform structure, often have regional inhomogeneities, which may be present on scales of hundreds of microns or smaller and are not easily identified by visual examination [11,12]. Therefore, “spot” analysis (even on micrometric scales) can result in misleading compositional information of an object under study. In contrast to these point analyses, the newly-developed scanning XRF system can examine up to  $400 \text{ cm}^2$  regions of a studied object, providing a far better understanding of a material's composition. The elemental maps are also a useful guide when single spot analyses are required, because maps allow for choosing the most suitable areas for point-based analysis, overcoming the problem of regional inhomogeneity. In addition, by working in this manner, the required number of single spot analyses can be reduced, saving working time for both data acquisition and analysis.

The XRF elemental mapping can be complemented with other mapping techniques, in particular, technical photography [13] and multispectral imaging [14] which can be implemented with relatively low-cost systems.

Thanks to our collaboration with the Opificio delle Pietre Dure (OPD) [15] in Florence, we have had the special opportunity to analyze many

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masterworks, among which are paintings from the “Old Masters”, such as the famous Italian Renaissance artist Raffaello Sanzio. Here, primary results from measurements performed with our XRF scanner on “The portrait of a young woman” (Fig. 1) are reported, in order to point out how an imaging approach can help solve ambiguities, discover hidden details, such as *pentimenti*, and identify areas to be analyzed to extract information representative of the object.

## 2. Material and methods

The masterpiece under study is an early example of Raffaello's maturity. “The portrait of a young woman” (Fig. 1), also known as “La Muta”, is an oil panel ( $64 \times 68 \text{ cm}^2$ ) painted in between 1507–1508.

This masterpiece, usually located in the Galleria Nazionale delle Marche (Urbino), was temporarily moved to the OPD for restoration. Over time, xylophage insects had caused extensive damage [16,17] not only inside the panel, but also to its surface, leading to a lack of support for the pictorial film and in some cases, to its total detachment.

After the panel's structure had been reconsolidated, for restoration of the painted surface it was important to understand the composition of the pigments used by Raffaello. For this reason, before the restoration an extensive multi-technique diagnostic campaign was carried out [18]. Thanks to the elemental imaging, it was possible to determine not only the general composition of the painting, but also to find “hidden” features such as, for example, *pentimenti* (underlying paintings in the artwork, evidence of revision by the artist).

The scanning system used during this diagnostic campaign is a prototype [10], developed at LABEC, improving on the previous spectrometer, which only allowed for single spot analysis [19–23].

The whole system consists of a measuring head, three high-precision linear stages, a waveform digitizer, a radiation safety system and a control PC.

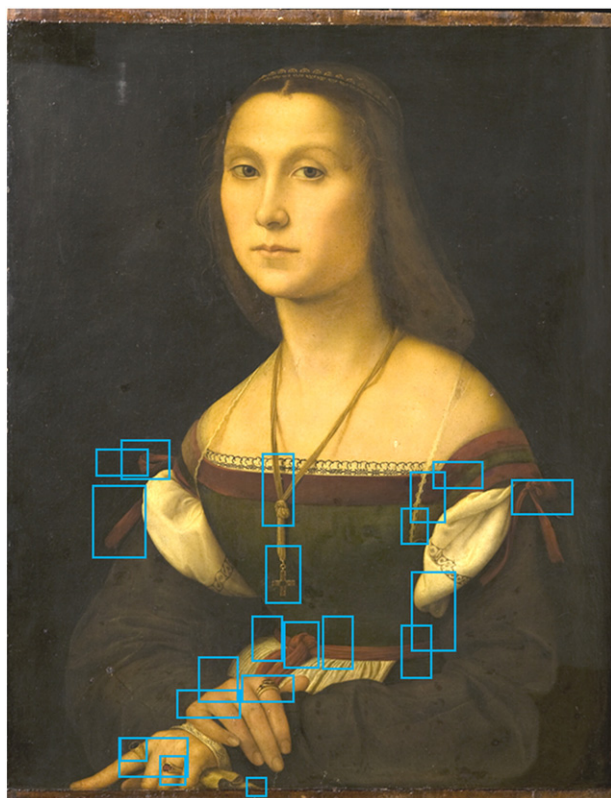


Fig. 1. “Portrait of a young woman”. Blue squares highlight the investigated areas.

The measuring head incorporates a cooled X-ray tube (Moxtek©) with a Cr anode (40 kV, 0.1 mA, 0.8 mm beam spot size on the sample), an SDD detector (Amptek©) and a webcam coupled with two lasers, which guarantee positional reproducibility and control on the working distance (Fig. 2). The head is mounted on high-precision three-axis linear stages (M404PD-Physik Instrumente©) (Fig. 2). This arrangement allows for information acquisition over an entire area: during an areal scan both the X-ray spectra and the corresponding spatial coordinates are recorded, thus permitting one to obtain elemental distribution maps. The software used for acquisition, scanning, and moving control has been developed by the authors on the Qt (Gnu General Public License) open source platform [24]. This choice allows us to easily adapt our software to different hardware (e.g. detectors) or diverse experimental conditions, what would be impossible using proprietary data acquisition or control software. For example, this very same system is exploited for the wide area imaging at the LABEC external microbeam, where the sample is raster-scanned under the fixed microbeam, so allowing to obtain elemental maps with micrometric ( $\sim 10 \mu\text{m}$ ) spatial resolution over surfaces as wide as  $20 \times 20 \text{ cm}^2$  [25].

The system can be easily customized by changing the maximum size of single maps (up to  $20 \times 20 \text{ cm}^2$ ), the X-ray tube anode (which allows optimizing detection efficiency for diverse energy regions) and collimators ( $300\text{--}1000 \mu\text{m}$  typically) for optimal beam spot size depending on sample granularity. In air, the spectrometer allows for easy detection of all elements down to  $Z = 14$ . By using a continuous helium flow along the path of the X-rays emitted from the sample (between target and detector), it is even possible to detect elements as light as sodium. In this particular study, it was not possible to use He for the measurements and the lowest possible detectable element was silicon.

In order to increase compactness and flexibility of the system, new developments are ongoing, i.e. further miniaturization of the system and an automatic system to keep constant the distance between the sample surface and the measuring head of the spectrometer.

XRF analysis was conducted over twenty-one areas (shown in detail in Fig. 1), selected in agreement with the restorers, in order to obtain deepened information about the painting palette and *pentimenti*.

The corresponding elemental maps ( $240 \text{ cm}^2$ ) were acquired in 6 h and 42 min. For all measurements, the standard conditions were: 35 kV anode voltage, 100  $\mu\text{A}$  anode current,  $1 \text{ mm} \times 1 \text{ mm}$  pixel size, and 1 mm/s scanning speed.

## 3. Results and discussion

To illustrate the efficacy and versatility of the new XRF system as applied to CH studies, we report some of the main results from the analysis of “La Muta”.

For each element, colors in the map are attributed as follows: first,  $M$  and  $m$ , respectively the maximum and the minimum number of counts of the element in the area under study, are determined. The  $(M-m)$  interval is divided into 256 sub-intervals, colored from black ( $m$  – color n. 1) to red ( $M$  – color n. 256). As a consequence, the same color in different maps may correspond to different counts.

### 3.1. Preparation layer, imprimatura, light and shadows and pigment identification

As seen in Figs. 3, 4 and 5, there are variations in the Ca distribution within every selected area. Ca shows higher absorptions in correspondence of higher  $Z$  elements. Indeed, heavier elements absorb Ca X-rays, producing a sort of “negative image” of the analyzed area (this behavior is particularly evident in Fig. 3 where the Ca counts almost vanish in correspondence to the hand, characterized by high content of Pb). This behavior suggests the existence of a painting preparation layer, most probably composed of gypsum ( $\text{CaSO}_4$ ), which was standardly applied to produce a hard smooth surface for panel paintings at Raffaello's time [26–28].

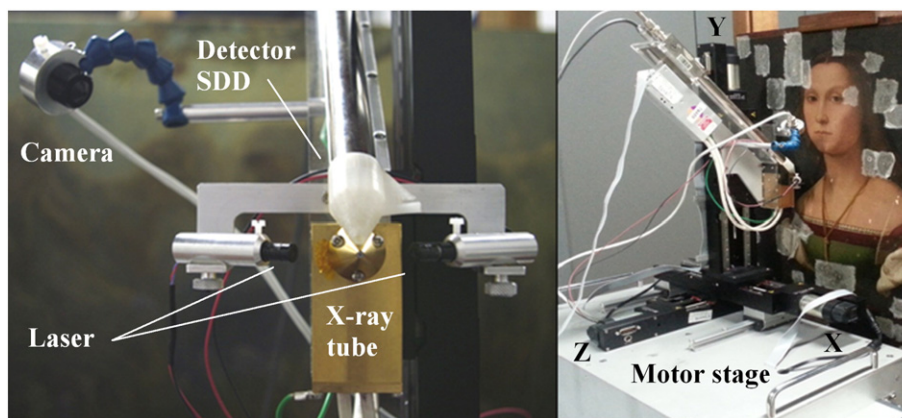


Fig. 2. XRF scanning system setup of the measuring head mounted on the three axis motor stages.

Similar considerations can be made for the Pb maps of high ( $L\alpha$ -line – 10.55 keV) energy and low ( $M\alpha$ -line – 2.3 keV) energy. As shown in Figs. 3, 4 and 5, the formers are by far more homogeneous and intense than the latters.

This difference can be explained considering that the low energy Pb-M X-rays are absorbed practically by any overlying pigment (especially in cases of thick or high-Z applications). This means that, if the Pb M X-rays are detected, they originate from a shallow layer, while if only the Pb L lines are detected, the Pb contribution must arise from a buried layer. The presence of this element typically indicates the use of lead white pigment ( $2PbCO_3 \cdot Pb(OH)_2$ ) [25,29,30]. Synthesizing, the inter-comparison between L- and M-line maps indicates that lead white pigment was applied at two different depths, in both a deep layer (imprimatura) and in a shallower pictorial layer. Imprimatura came into standard use during the Renaissance, particularly in Italy. It indicated a color layer used to create a ground for a painting according to the classical technique [25,31,32]. The imprimatura over a toned gesso or a toned primer reflects the light through the overlaying painting layers, almost creating a 3-D effect.

Overall, identifications of pigment depth and variation provide a concrete example of the scanning XRF's versatility and efficacy for studies of CH. These features provided by elemental imaging are a unique

benefit of the scanning system and it would be hard, if possible, to achieve similar results with single-point measurements, spending longer measurement time and with higher uncertainty.

To further demonstrate the strengths of the XRF scanner, we can observe other elemental maps from the same pictorial area. On the panel's surface, the skin tone is characterized by roughly uniform distributions of Pb (M line) and Hg, suggesting the use of lead white pigment with small amounts of cinnabar (HgS) [25,33,34].

Turning our attention to the woman's rings, we notice overlapping distributions of Sn, Pb, Fe and K. The simultaneous presence of Sn and Pb suggests the use of tin-lead yellow pigment ( $Pb_xSnO_x$ ), formally known as "giallorino" [25,35,36]. Additionally, coherent distributions of Fe and K usually occur in the presence of ochre (iron oxide(III)) [25,37,38], where K could be found as a trace element. This comes as no surprise, as ochre was widely used during Raffaello's lifetime, and throughout the Renaissance as a whole. So we can assume that Raffaello probably mixed giallorino and ochre pigments to obtain his unique "gold" color.

In Fig. 4, the distributions of Fe and K are only partially consistent; indeed the higher K signal has a behavior similar to that of Hg, suggesting the use of a rich-K compound in mixture with cinnabar (see Section 3.3 for a more detailed discussion).

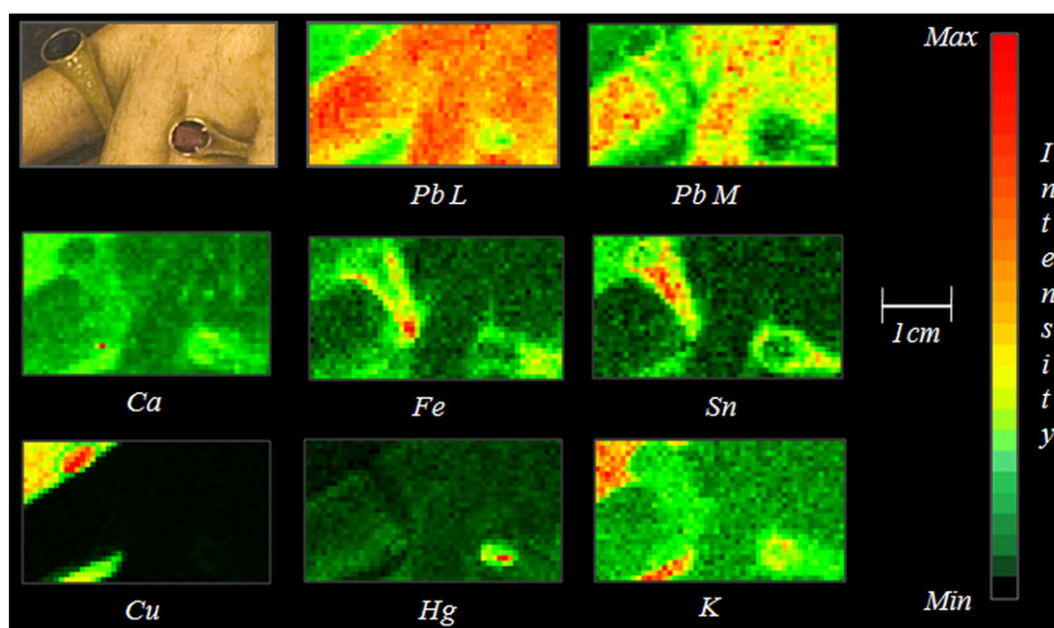


Fig. 3. XRF elemental maps detailing the hands and rings of La Muta. Observed are numerous elements which are each indicative of different pigments used: Pb (high energy (L lines) and low energy (M lines)), Ca, Hg, Cu, K, Sn and Fe.



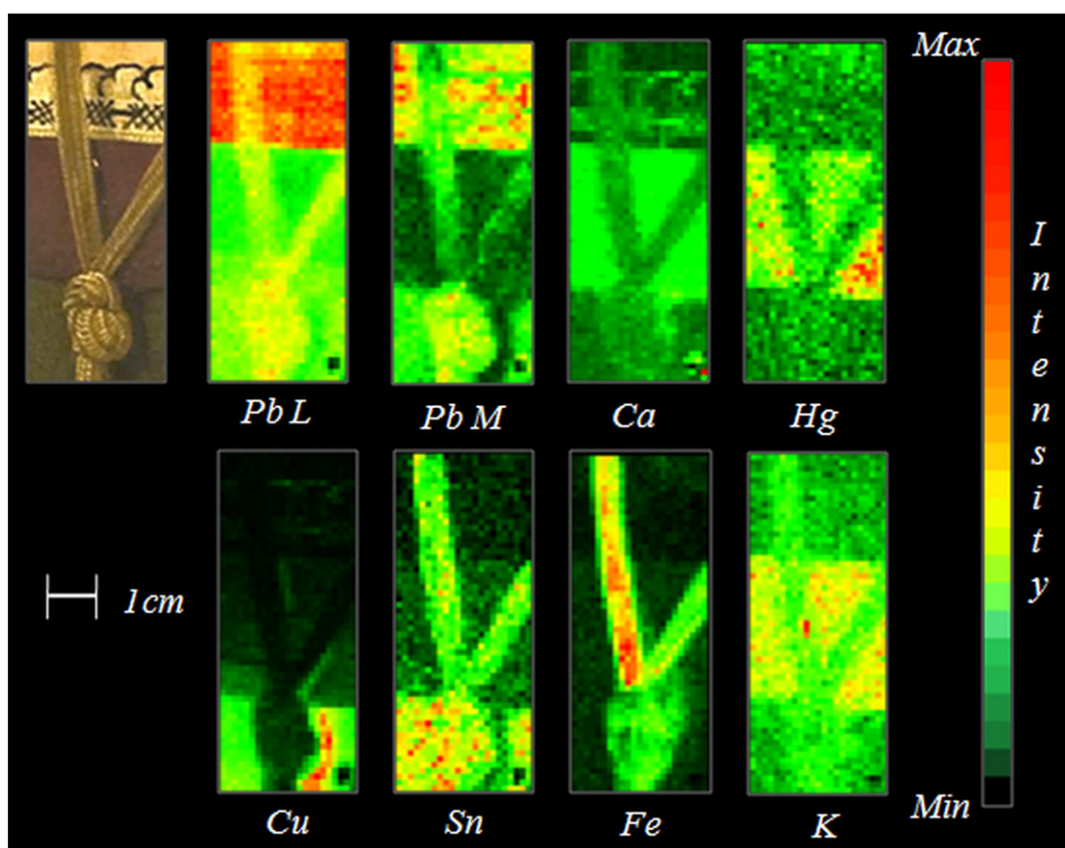


Fig. 4. XRF elemental maps detailing the bodice, in correspondence with the necklace. The elemental maps include Pb (high energy (L lines) and low energy (M lines)), Ca, Hg, Cu, K, Sn and Fe.

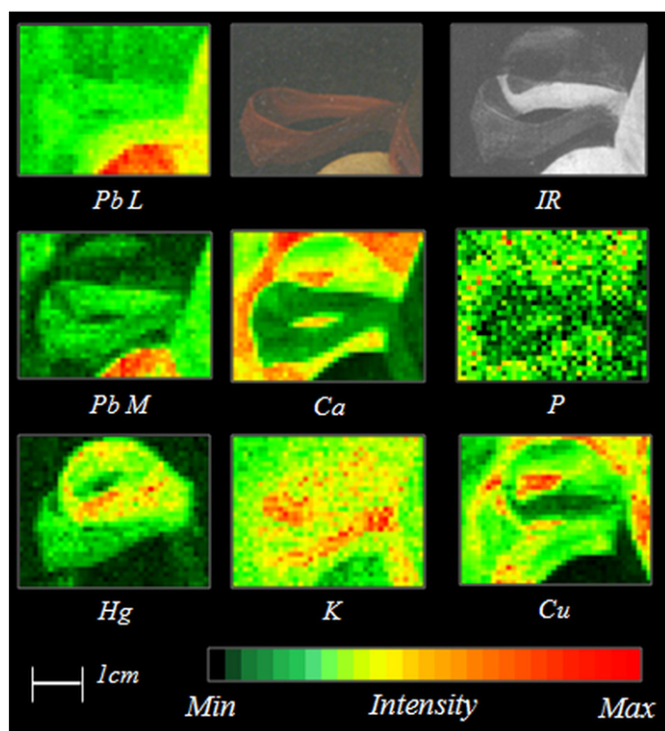


Fig. 5. XRF elemental maps detailing the area surrounding the bows: shown are the results for Pb (high energy (L-line) and low energy (M-line)), Ca, Hg, K and Cu. Also shown is an IR analysis of the same area, acquired by the INO (National Institute of Optics) group, which was used as a guide.

The signal distribution of iron (Figs. 3–4) corresponds to darker areas in the panel, suggesting the use of ochre for shadow on the rings, around the edges of the fingers and in the right side of the necklace. Conversely, the brighter parts of the rings exhibit higher Pb-M intensities, indicating the addition of lead white to the overall pigment.

Furthermore, the Cu map in Fig. 4 shows a clear correlation with the green region, thus suggesting a copper-based pigment [25,39], although XRF (as an elemental technique) is not able to discriminate among the variety of pigments that could have been used by Raffaello, such as Verdigris ( $\text{Cu}(\text{CH}_3\text{COO})_2$ ) or Malachite ( $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ ) [40–42]. In the same area we also observe the simultaneous presence of Sn and Pb, suggesting that Raffaello painted this section using a mixture of “giallorino” and a copper-based pigment, obtaining a warm green.

### 3.2. Black pigment identification

In Fig. 5, the black background is denoted by high counts of Cu, Ca and Pb. The last two elements were due to the preparation layer (gypsum) and imprimatura (lead white) respectively, as previously mentioned. Therefore only the copper signal is characteristic of the black background. For this reason we can hypothesize that Raffaello created this shade by mixing a copper-based pigment with a black pigment. Generally, XRF analysis is unable to discriminate among a multitude of black pigments, most of which are organic compounds.

However, a noticeable exception is bone black [43,44]. This pigment, obtained by charring animal bones, consists of 15–20% carbon and 60–70% calcium phosphate. So, unlike the majority of organic black pigments, bone black may be identified by XRF analysis as it is characterized by signals of Ca and P. In this particular case by means of single point XRF analyses, the identification of bone black pigment would be

hard, if possible, because the Ca signal due to the pigment is indistinguishable from that due to the preparation layer ( $\text{CaSO}_4$ ). In addition phosphorous, the other marker of bone black, has X-rays of too low energy (2 keV) to be normally detected.

The new scanning system allowed us to effectively point out its presence. We focused our attention on the lace embroidery area (Fig. 4), where it was possible to distinguish the calcium signal of the pigment from that of the preparation layer. The upper part of this area is characterized by high lead counts, which suggests the use of lead white in the lace shirt and in the skin. This high-Z element strongly absorbs the low energy Ca X-rays (3.69 keV) of the preparation layer, as clearly visible in the Ca map. However in correspondence of the black embroidery the Ca map shows a noticeable increment of counts. This behavior can be explained only assuming both that Ca is in the black pigment of the embroidery and that this pigment is in a shallow layer.

Elemental maps in Fig. 4 show that the composition of the black lace embroidery is characterized by Ca and also Cu (the P signal in the spectrum is statistically significant, confirming the presence of this marker, but counts per pixel are low and P map is hardly readable). This provides strong evidence that both this lacing and the panel's background were painted with a mixture of bone black and Cu pigments.

### 3.3. *Pentimenti*

As already mentioned, *pentimenti* are “hidden” features of the painting, which represent the evidence of revision by the artist. In this masterwork many underlying paintings were discovered thanks to Infrared Reflectography, such as in the bows, in the shoulder of the lady's dress or in the hands; all of them were characterized by XRF scanning analyses, although not reported here for brevity.

Fig. 5 showcases one example of these *pentimenti*, where the elemental maps of Pb (low energy), Ca and Hg reveal the presence of two bows — one visible and one hidden.

These elemental maps are in good agreement with results obtained by multispectral analyses (Infrared Reflectography) [45,46], providing in addition information about the bows' pigment composition.

Both bows are characterized by strong Hg lines, which suggest Raffaello's use of cinnabar ( $\text{HgS}$ ). Additionally, where the two bows

overlap, Hg intensity increases. The image exhibits similar behavior in the infrared, being brightest in the regions where the bows overlap.

Comparison between the Hg and Pb maps highlights compositional differences among the two bows. The “hidden” ribbon shows higher intensity of Hg than the “visible” one, which is instead characterized by higher Pb content, as shown by both maps and spectra (see Fig. 6).

The addition of lead white could be motivated by the need of increasing the opaqueness of a semi-transparent red color (different from cinnabar, see later), as the “visible” bow was painted directly upon the black background (as we can see from the Cu map in Fig. 5).

In the ribbons, we also notice the presence of K. This might indicate the use of ochre, as previously mentioned. To further investigate the possible existence of ochre pigments, we performed single-spot analyses, utilizing the elemental maps as a guide for choosing representative points. Single-point spectra for both the visible and hidden bows (Fig. 6) contained a large K peak. However, for each of the two bows, K signal is higher than that of Fe, almost negligible. Since Fe is the principal element in ochre, this evidence suggests that Raffaello didn't use these pigments to paint the bows. An ochre-based spectrum would be characterized by a large Fe peak with only a trace amount of K, the opposite of what was found. These results indicate that another potassium-containing compound must have been used in the painting, mixed together with cinnabar. From this, we hypothesize that “La Muta's” ribbons contain K–Al sulfate, known historically as “allume di rocca” ( $\text{KAl}(\text{SO}_4)_2 \cdot 12(\text{H}_2\text{O})$ ) [47]. This compound was commonly used as a mordant for organic red lake (semi-transparent color) [48,49]. Unfortunately, we can only infer the existence of potash alum by the spectrum's K peak, as characteristic Al emissions are of too low an energy to be detected by in-air XRF analysis (as already mentioned, it was not possible to use He). However, on the above mentioned results, we suggest that both ribbons were painted mainly with cinnabar and red lake, with the “visible” bow further characterized by the addition of lead white.

Also of interest, we observe a more intense Ca distribution in the “hidden bow” for both the elemental maps (Fig. 5) and the single-point spectra (Fig. 6). This can be explained in the very same way as discussed for the black lace embroidery. An overlying layer of black pigment obscured the “hidden bow”; both bows are distinguished by Hg, an element which absorbs the lower energy (3.69 keV) Ca X-rays from the preparation layer. This is clearly occurring in the “visible bow”,

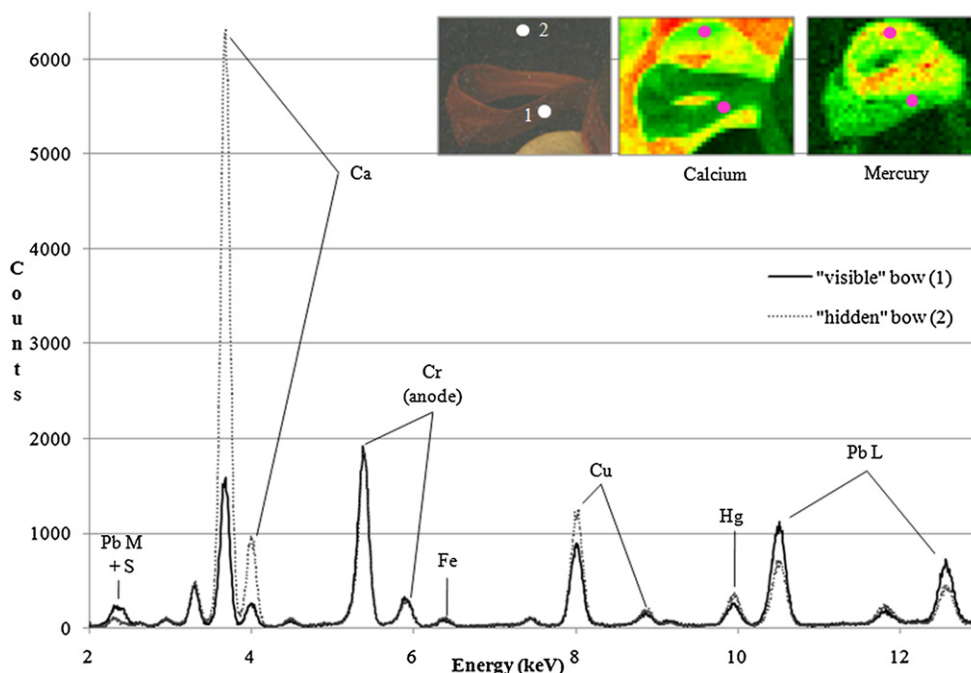


Fig. 6. X-ray spectra acquired for the “visible” (1) and “hidden” (2) bows.

**Table 1**

Colors used in "Portrait of a young woman", their characteristic elements and the corresponding pigments, as suggested by the authors.

Color	Characteristic elements	Pigment
Green	Cu, Sn, Pb	Green-copper based pigments (malachite, Verdigris, etc.) and tin-lead yellow
"Gold"	Pb, Sn, Fe	Lead white, tin-lead yellow and ochre
"Incarnato"	Pb, Hg	Lead white and cinnabar
Red	Hg, K	Cinnabar and red lake
White	Pb	Lead white
Black	Ca, P, Cu	Bone black and a copper based pigment
Darker areas (shadow)	Fe, K, Ti	Addition of ochre
Brighter areas	Pb	Addition of lead white

that shows very little Ca content. Therefore the Ca enrichment in the "hidden" bow mainly comes from the topmost layer, bone black surface.

X-ray lines of P, one of the markers of bone black, have very low energy (2 keV) and thus the P contribution is only due to the topmost black layer. In addition its spatial distribution in the whole area, with the exception of the interior of the "visible" bow, actually confirms the previous results about the use of bone black.

The spatial distributions of Cu, Ca and K largely overlap, which strengthens the hypothesis of a mixture of bone-black and copper-based pigments for the black color, both in background and in the details (embroidery, etc.).

The other scanned areas further confirmed Raffaello's use of cinnabar, giallorino, ochre, bone black, red lake, copper, and lead white pigments. This information is summarized in Table 1.

#### 4. Conclusions

The XRF scanning system, newly developed by the LABEC in collaboration with the INFN network for CH studies (CHNet), proved to be very promising. By providing up to  $20 \times 20 \text{ cm}^2$  elemental maps of a surface, the scanning system is more versatile and more efficient than previous, fixed-head designs. Additionally, using elemental maps as a guide, one can precisely identify points on a sample's surface ideally suited for more detailed analyses. In this way, one can easily focus on representative points.

This range of benefits and handy applications to CH is clearly evidenced by this study on Raffaello's "La Muta." The scanning XRF system was used to obtain elemental maps from diverse areas across the painting's surface. Our identification of bone black pigment in "La Muta" was only made possible by comparing distributional maps of different elements. Furthermore, using the areal maps to identify an instance of *pentimenti*, we performed spot analyses on the painting's two ribbons, one being visible and the other hidden beneath the surface. By carefully contrasting both point and areal maps, we were able to find difference in pigments composing the two ribbons, while also identifying the use of red lake. In addition, pigments used by Raffaello were easily identified, as maps allowed us to choose the most suitable areas for point-based analysis, overcoming the problem of local inhomogeneity.

Our analysis of "La Muta" clearly demonstrates the potential of the scanning XRF as applied to studies of Cultural Heritage. The system allows for efficient and multifaceted analysis of a sample's composition, offering insight that would be difficult, if not impossible, to acquire through point-based XRF studies. Future applications of the system would provide new knowledge to the CH community.

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