XRF and reflectance hyperspectral imaging on a 15th century illuminated manuscript: combining imaging and quantitative analysis to understand the artist's technique

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XRF and reflectance hyperspectral imaging on a 15th century illuminated manuscript: combining imaging and quantitative analysis to understand the artist's technique

Laurence de Viguerie[1*], Sophie Rochut[1], Matthias Alfeld[1], Philippe Walter[1], Sophie Astier[2], Valérie Gontero[3] and Florence Boulc'h[4]

Abstract

We present here the combination of in situ non invasive techniques to investigate a precious 15th century illuminated manuscript of Petrarch's work, *De remediis utriusque fortunae* held in the Méjanes library in Aix-en-Provence (France). X-Ray fluorescence spectroscopy, mapping and point analysis, and visible reflectance hyperspectral imaging allow an unprecedented analysis of this manuscript. They provide new clues for its attribution by revealing a partly hidden coat of arms and describing the illuminator's palette and techniques in detail. We reveal the identity of the first possessor of this manuscript, Tanguy IV du Châtel, known as a 15th century bibliophile close to Louis XI. This information is a further element contributing to the attribution of the richly illuminated folio 6 of this manuscript to François Le Barbier. Pigments and dyes used for this folio have been investigated with particular emphasis on the study of the superimposed colours thus providing a better understanding of the artist's technique and know-how.

Keywords: Medieval illumination, Chemical imaging, Quantitative analysis, Visible reflectance

Introduction

In 1366, Petrarch wrote a major work, *De remediis utriusque fortunae*, at the crossroads of morality, philosophy and religion. It is a collection of *exempla*: each chapter presents a specific situation, and explains how to react when faced to fortune, in the first book, or misfortune, in the second book. The text is a series of questions and answers between pairs of allegories—Reason, Joy and Pain—discussing various subjects: for example, in the first book, the finding of a treasure; in the second book, being in bad health or losing one's wife. In 1378, Jean Daudin, a canon, received from Charles V 200 francs for

his translation in old French of Petrarch's text, with the title *Les Remèdes de l'une et l'autre Fortune* (*Remedies from Fortune Fair and Foul*). This translation includes eight well-known manuscripts, dated from 1470 to 1480; one of them (Ms. 1800, 275 ff., 354 × 265 mm) is held in the Méjanes library, in Aix-en-Provence (France). Precious manuscripts traditionally exhibit a miniature at the *incipit* of the text or/and at the beginning of each section. In the manuscript from Aix, two miniatures are used to illustrate the text, but unfortunately the second one is missing. The remaining miniature, in folio 6, is all the more precious now that its pendant has disappeared. Folio 6 (Fig. 1a) is the beginning of the first book, *Remedies against Fortune*. It is richly illuminated and features a half-page framed miniature and decorations in the margins and initial. A coat-of-arms is also present but partly covered with red paint. These decorations are close in

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Fig. 1 **a** Folio 6 of *De Remediis utriusque fortunae* manuscript (Aix en Provence, Bibl. mun., ms 1800); Maps created with spectral angle mapping algorithm displaying spatial distributions of endmembers. **b** semi-automatic data treatment, **c** SAM performed with chosen spectra of colours in the miniature shown in **d** dark background, white, green, brown/gold, red, violet, blue. The tolerance angle is 0.15 rad. The rotation stage induced a slight deformation visible here

style to those executed by the workshop of the Parisian illuminator François Le Barbier, father, previously known as "Maître François". This can be seen if it is compared with a well-identified manuscript (*De Remediis* held in the National Library at Vienna) which features the same composition in its illumination. This similarity was also proposed by *the French Institut de Recherche et d'Histoire des Textes (IRHT)*. However, the attribution of the manuscript in the Méjanes library in Aix-en-Provence to a workshop is still open.

We aim to bring new insights to this question from chemical analyses. As sampling can be dangerous for so delicate a work of art, a non-invasive approach was the only option. The identification of the medieval organic and inorganic pigments by reflectance, Raman and X-ray fluorescence spectroscopies is now relatively straightforward [1]. More recently the use of imaging techniques [2–7] has been demonstrated and discussed on such precious art objects: it is now possible to identify pigments and map them. The successful combination of MA-XRF scanning and reflectance hyperspectral imaging can be of great help for pigment identification in illuminated manuscripts, providing in some cases new clues about their origin or even the identity of the illuminator [3]. Several 15th century French manuscripts have been studied by

different groups: among them, the Book of Hours of the Parisian *maître Boucicaut* [8] and later, three Books of Hours preserved in the *Palacio Nacional de Mafra* [9], all based on point analyses and reconstructions. The results highlighted characteristic French traditional practice such as the use of Brazilwood red lakes in glazes.

For our investigation into the manuscript from Aix (Ms. 1800), we combined visible/near infrared (400–1000 nm) reflectance spectroscopy to X-ray fluorescence spectroscopy. We used imaging techniques as well as point analyses with quantitative data treatment, with a particular emphasis on the study of the mixtures and superimposed colours, to go deeper into the understanding of the different materials.

Experimental
The miniature
The folio 6 (Fig. 1) is the beginning of the first book, *Remedies against Fortune* with a half-page framed miniature featuring Fortune. Her wheel became famous thanks to Boethius in the 6th century. In his *Consolatio Philosophiae*, the poet describes the four positions on the wheel, as the four cardinal points, representing the changing fortunes of life, summarized in the quotation: *regno/regnavi/sum sine regno/regnabo (I reign/I reigned/I am*

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without kingdom/I will reign). The painting shows, in Ms. 1800, an allegory of Fortune, its wheel and a group of people in a large room that looks like a church. A king is seated on the top of Fortune's wheel. She is holding a crank in her right hand, and may turn it at any moment. Members of the surrounding audience are waiting to take the king's place: men and women, young and old, lay and religious people. Most of them open their hands before Fortune: by this gesture, they accept the rules of the wheel. Fortune is dressed as a noble lady of the time; her face is half-white, half-dark, a particularity that originates in Boethius' iconography. With her left hand, she points to a text in a cartouche: '*Fortune suys, royne et deesse, A quy monstre ma belle face. L'ung lui fait dons, l'autre promesse. Tous l'honnorent, chascun l'embrasse*'. ('*I am Fortune, queen and goddess, now I show my nice face. Some people give gifts to her, others promise. Everybody honours her, everyone embraces her*'). Facing the scene, a man dressed like a clerk is represented writing a book: it is the medieval traditional painting of the author at work, that is to say Petrarch writing *De Remediis*.

Spectroscopic studies

The manuscript was investigated by a VNIR hyperspectral camera by Specim (Oulu, Finland). The camera was mounted on a rotation stage to acquire the images in push broom technique, i.e. by scanning the manuscript horizontally and acquiring full spectral information for one vertical line on the manuscript at a time. The spectral range was 400–1000 nm with 212 wavelength channels (rebinned from 1200) with a spectral sampling of 2.8 nm and 1600 spatial pixels. Two objectives were used. With the first one (OL17, Specim, focal length 17 mm), one image of the entire miniature was acquired with a spatial sampling of approx. 250 μm at a camera-manuscript distance of 62 cm. The scan was acquired with 50 ms integration time, 6 fps (frames per second) and 0.01/s rotation speed. With the second one (OL50, Specim, focal length 50 mm), smaller zones were imaged with a spatial sampling of approximately 40 μm. In this "zoom" configuration (distance camera-manuscript of 40 cm), the acquisition parameters were 200 ms integration time, 4 fps and 0.07/s rotation speed. During the investigation, diffuse illumination is provided by three 20 W halogen lamps, placed at 0.4 m away. The data was normalized with dark and bright field images using the Specim plug-in in ENVI (Harris Corporation, Melbourne, Florida, USA). To check the quality of the reflectance image cube the reflectance spectra from the white and black diffuse reflectance standards placed in the image scene were examined: they showed in the range between 450 and 900 nm a noise level of 1.7% reflectance for the white reference and 0.5% for the dark reference.

An in-house-built XRF instrument was used, featuring a Pd anode end window X-ray tube (Moxtek MAGNUM, Orem, UT) operated at 30 kV and 50 μA and a silicon drift detector (X-123FAST SDD, Amptek, Bedford, MA) with an active area of 25 mm^2 collimated to 17 mm^2 and a nominal thickness of 500 μm. The X-ray tube was connected to the detector via a holder produced by 3D printing (fixing the angle between both to 45° for single point analysis, or 32° for imaging). As a collimator primary optic, a Pd tube of 800 μm inner diameter was used, yielding a beam size of approximately 1.2 mm. The typical working distance is 1 cm. A digital microscope (Dino-lite, AnMo Electronics Corporation, New Taipei City, Taiwan) and a laser distance measurement device (OADM20, Baumer, Frauenfeld, Switzerland) allow for measuring the position of the primary beam on the surface of the object. The system was used with manual translation stages for single-point analysis with acquisition time of 300 s. For XRF imaging the measurement head was mounted on a motorized XY stage with 20 cm travel range in both directions (M-403.8PD, Physik Instrumente (PI) GmbH & Co. KG, Karlsruhe, Germany) with an additional manual Z translation. The motorized stage was fixed to a three-axis manual rotation stage mounted on a photography tripod. In this configuration the primary beam impinged in a normal angle on the surface sample with the detection angle being 58°. The limits of detection were estimated from a NIST SRM 610 reference as described elsewhere [10]. For a 300 s measurement they were found to be between 120 ppm (Ca, Z = 20) and 22 ppm (Cu, Z = 29) for elements heavier than Ca (Z = 20). The instrument has been previously described elsewhere [11].

For the evaluation of the raw, full spectral XRF data, the PyMCA software was used [12]. As we have previously demonstrated, PyMCA allows one to estimate the concentrations and/or layer thicknesses of cultural heritage samples based on fundamental parameter calculations. We successfully applied this approach with a portable XRF system (featuring a polychromatic X-ray tube) on glass standards and an Egyptian faience [13]. Further, we used it on multi-layer reference samples on a 16th century easel painting [14]. Fundamental parameters were taken from the internal database of PyMCA, geometrical parameters were directly measured and instrumental parameters obtained from the instrument description and refined by the measurements of reference materials and a metallic Pb sample (flux 3.4×10^7 photons/s, time 300 s, detector active area 0.25 cm^2, distance 2 cm) [13].

The result of these fundamental calculations is an areal density (the product of thickness and density) of the layers, so that in order to derive its thickness the density needs to be estimated. This is based on the known

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composition of the pigment and adjusted for the presence of organic binders. In the case of brazilwood, a gypsum substrate has been considered. The density of lead white (or vermilion) layers is defined as 3 g/cm, and the one of lapis and brazilwood lake as 2 g/cm to take into account the mixture of the pigment with the binder. The thickness of the layers used for the fundamental parameter calculations is manually modified by the user until good agreement between simulation and measurement is achieved.

Macrophotographs (Olympus OM-D E-M5 Mark II with a Olympus 60 mm macro lens) of the analysed areas were also taken.

Data treatment methodology

As the amount of data obtained from hyperspectral measurements is huge, statistical methods were carried out to reduce the size of the data cube in ENVI. We used the spectral angle mapper (SAM) algorithm to cluster the spectra of the data set according to their similarity to endmember spectra (Fig. 1b, c). Endmembers are extreme data points that cannot be represented by any positive linear combination of other spectra in the data set.

A first set of endmembers was derived by using the 'Spectral Hourglass Wizard' of ENVI, which performs an MNF-PCA transformation (Minimum Noise Fraction-Principal Component Analysis) on the data. The extreme points of this distribution were identified calculating the pixel purity index (PPI) for all pixels and selecting the 10,000 most extreme ones. In a multi-dimensional visualization, endmembers were manually selected. The resulting spectral angle map is shown in Fig. 1b. This approach has been described in detail by other groups before us [2].

This approach provided an overview of the distribution of pigments, but not all endmember spectra were representative for the pixels associated to them, allowing one to identify individual pigments or mixtures thereof. Therefore, taking these results into account, pixels representing pure pigments were selected from the data set and used as endmembers for the SAM (see Fig. 1c, d).

The SAM maps were used as a guide to select areas for investigation by XRF spot analysis. The information provided by XRF and reflectance spectra were used to identify the composition of mixtures.

To investigate specific effects such as shadowing or highlighting, or to investigate details with a high degree of precision, we acquired hyperspectral images with a 40 μm spatial sampling as well as XRF maps. Here also the SAM images were used as a guide to select zones of interest. However, the entire surface of the Folio could not be investigated by these detailed methods as the time

for the investigation of the manuscript was limited, and the curved surface of the page required a manual adjustment of the instrument object distance that was not practical for larger scans.

To answer specific questions on the artist's and his workshop's technique (the thickness of gold layers, the presence of preparation layer…), quantitative data treatment of the XRF spectra, as discussed above, taking the layered structure of the sample into account, were required. The penetrative nature of X-rays allows one to record fluorescence signals from layers present below the surface. This can complicate the data evaluation as it is not in all cases clear if an element is present in a pictorial or a preparation layer. On the other hand, XRF was for the same reason crucial for the identification of the partly hidden coat of arms at the bottom of the page. As is to be expected, given the low radiation doses used, no change or damage to the folio was observed after the experiment.

Although imaging and quantitative point analyses are very powerful, a complete interpretation could not be performed without a detailed visual investigation using macro-photographs of selected zones. Only these allowed one to observe the heterogeneity of the investigated area on a microscopic level, and thus helped to interpret the spectra correctly. Medieval receptacles and technical texts enabled us to clarify the analyses, and were a valuable help in the identification of mixtures. Four different texts have been consulted: (i) Theophilus' *Diversarum artium schedula* (12th century) translated by de l'Escalopier [15] (ii) the recipes of Antoine de Compiègne, Parisian illuminator, included in *Liber Colorum* (15th century) transcribed by Villela-Petit [16] (iii) the French critical translation by Déroche [17] of Cennino Cennini's *Il Libro dell'arte* (15th century) (iv) and Thompson's interpretation of Ceninno Cennini's 'manual' *The materials and techniques of medieval painting* published in [18].

Results and discussion
Overview images

In Fig. 1b–d the SAM maps of the Folio are shown. They feature clusters of similar reflectance spectra that largely corresponding to un-shaded colours, but not necessarily pure pigments. This provides an overview of the pigment use in the object that further guided our investigations. However, the dark background and the floor are hardly associated to a representative endmember.

The elemental maps acquired by XRF in Fig. 2 allow a straightforward visualization of subtle differences in peak intensities. They reveal an interesting co-localization of different elements (for example Ca and S, or Cu and Zn in green); however the results were difficult to interpret as only selected zones and not the entire page could be

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Fig. 2 XRF mapping of two selected zones of folio 6: **a** Fortune and **b** Petrarch at his desk
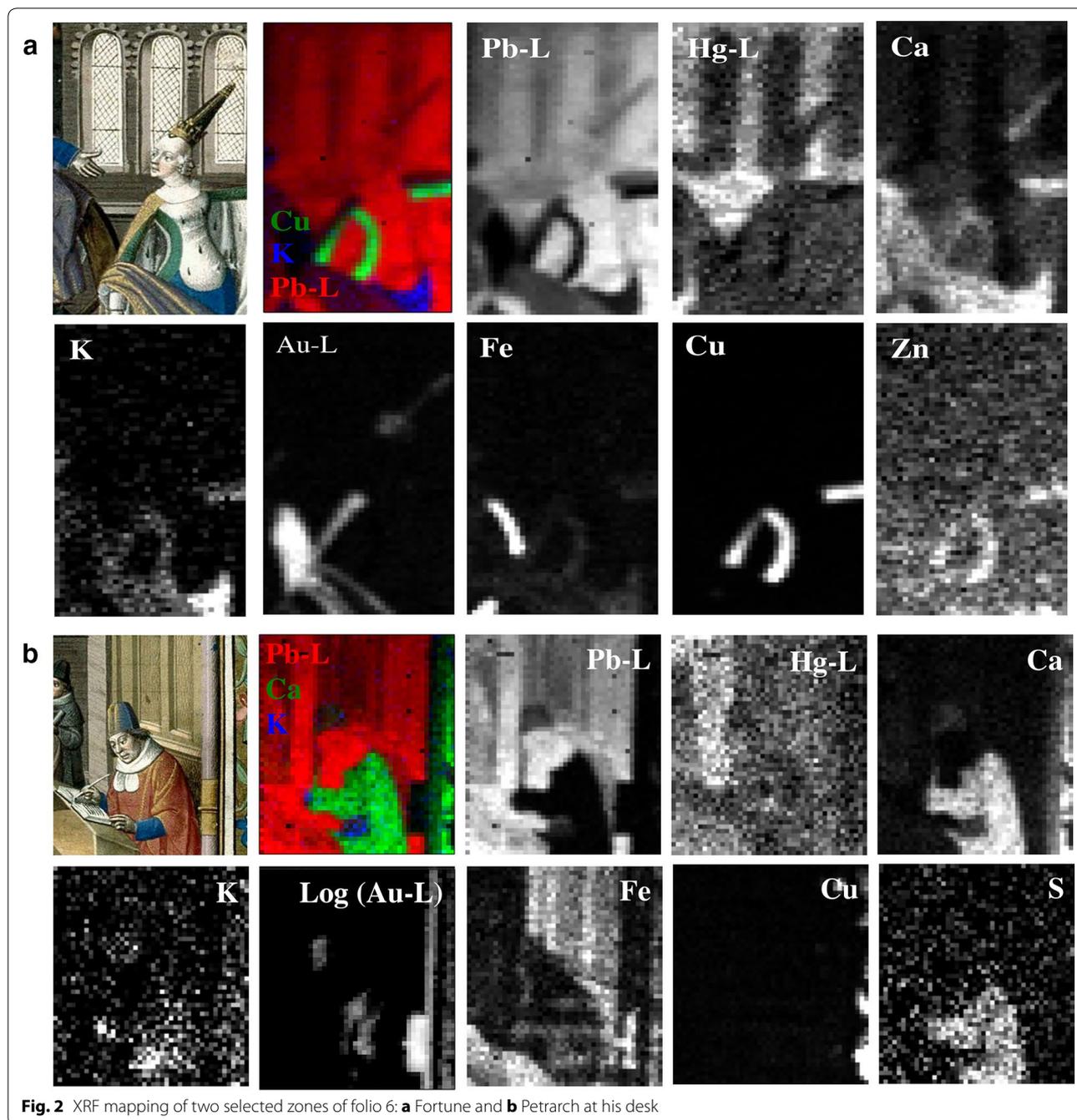
imaged. The use of lake pigments composed of dyes and light elements results in an absence of signal in central zones in which the pigments were expected.

Identification of the main pigments: qualitative analysis

The palette is consistent with what is known to be a 15th century miniature palette [8, 9]: brazil wood lake, vermilion in mixtures, lapis-lazuli, lead white, verdigris, ochre, gold, ink (possibly green earth also). Outside the miniature, pure vermilion and azurite have been used.

White

One XRF spectrum on the parchment was first recorded on an empty zone in the right corner, displaying the presence of elements such as calcium and iron, that belong to the parchment itself and/or its preparation: parchment

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used to be rubbed over with chalk and powdered pumice in order to make it 'take' the ink and colours.

On a medieval miniature such as this, a white area can be the result of applying a white pigment or simply using the white surface already present. In the representation of the window, the white drapery, the flesh and the floor, lead is present, indicating the probable use of lead white (lead carbonate), whereas the composition of the white background of the cartouche corresponds to the readings for parchment. We note that reflectance spectra alone do not allow one to differentiate between these: the map created after SAM treatment, displays the same colour for the white of the windows and of the background of the cartouche (Fig. 1b, c).

Lead white was also mixed with different colours/pigments—the green of the leaves for example—to lighten them. It is found present in all analysed points, except in the cartouche. Taking into account the macro-photographs (Fig. 3a), we are able to suggest that a first thin layer of lead white was spread over the entire surface. Known practices of the time and the techniques used here, allow us to make this hypothesis: in order to

prevent the danger of gold and colours flaking off the surface of the parchment, this was given a thin coat of lead white paint [17].

Red

Different pigments have been used to produce the red colours. The red drapery, in Petrarch's mantle for example, has been obtained with a red organic lake, probably on a very thin layer of lead white and vermilion (present in the wall behind Petrarch). The organic lake is assumed to be brazilwood lake due to the absorption feature in its visible reflectance spectrum (Fig. 4), with characteristic absorption maximum at ca. 555 nm [19]. XRF maps show the co-localization of Ca and S in these areas. We can suppose from this result that the lake pigment was prepared by precipitating it onto gypsum. The use of brazilwood was also observed during other investigations on French medieval manuscripts, and it seems that the use of brazilwood red lakes are characteristic of French 15th century miniatures workshops [20].

The *Liber colorum* contains one brazilwood lake recipe *Ad faciendum rosam* (*How to make a pink*) dictated by

Fig. 3 Macro-photographs of: **a**, **b** the decorative initial under the miniature (note that the size of the flower is around 4 mm); **c** the dress of Fortune and of (**d**) Petrarch's face (10 mm size)

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Fig. 4 Different hues on the red fruit. On the left: hyperspectral image, on the right: reflectance spectra of **a** the mantle of Petrarch (brazil wood), **b** the red of the fruit (vermilion), **c** gold on the fruit, **d** shadow on the fruit. It is important to note that red the fruit is 5 mm in diameter
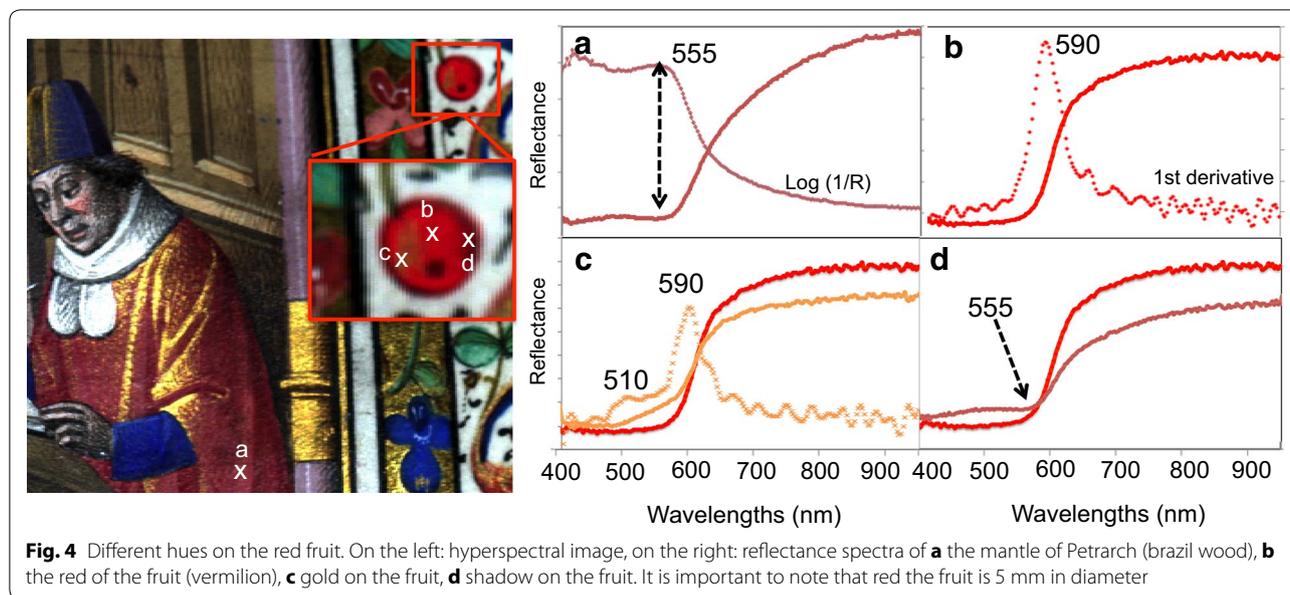
Antoine de Compiègne. The brazilwood should be first finely divided with a piece of glass. Two different dye extraction methods are recommended: old urine and lye. The colour of the resulting lake depends on the degree of acidity or basicity the solution. Indeed, Vitorino and et al. showed that different dye extraction methods resulted in different hues that ranged from light pink to dark red [21]. Alum and chalk were finally added to the extract before the mixture was heated for one hour. According to Thompson [18], chalk can be replaced by gypsum in order to produce a more opaque colour.

Vermilion (HgS) has also been used as a red colour. However, though it was known in the 15th century as a powerful colour of high intensity and as an excellent pigment in terms of quality, vermilion is only used, on one hand, in the miniature, in the form of a mixture with lead white and earth pigments to give a range of colours ranging from pink to brown, as described above. On the other hand, vermilion is used in the decorative margins (the red fruit for example in Fig. 4), and for the decoration of the initials.

Blue

The blue pigment used in the miniature for important figures such as Petrarch, Fortuna and the King has been identified as natural ultramarine obtained from lapis lazuli displaying maximum absorbance feature at 600 nm [19]. It is also used, as a small quantity added to lead white, to give a bluish tint to the floor. Its main component, the mineral lazurite $Na_6Ca_2[Al_6Si_6O_{24}]S_2$ is barely detected by XRF scanning as it contains mainly light elements (and Ca which is also present in the parchment).

However, it is important to remember that Afghan samples are the only ones characterized by lazurite crystals with high potassium contents [22]. It then often serves as a clue for the presence of lapis when detected in blue areas of illuminated manuscripts. The point analyses (with longer acquisition times, making it possible to better detect light elements) confirm this attribution: Al and Si are clearly seen, as well as K.

It is interesting to note that externally to the miniature, it is azurite $2CuCO_3, Cu(OH)_2$ that is detected thanks to the presence of Cu in the XRF spectra (with traces of As) and to its characteristic reflectance spectrum. It seems that the precious lapis lazuli was preferred for the main illustration whereas azurite was used on the other, less important, parts. Fortune's superior status is symbolically marked by the choice of precious pigments: gold for the wheel and to the frame of the cartouche to which she points, and ultramarine for her dress.

Green

The XRF spectra of green areas in the miniature and in the margins display a strong Cu signal. It can thus be related to either malachite $CuCO_3, Cu(OH)_2$ or to the 'verdigris' pigment which is an acetate of copper described as *especially good on parchment and very lovely to the eye*. Although the shape of the reflectance spectrum is quite broad, the maximum of absorbance would indicate the presence of verdigris rather than malachite [19, 23]. The medieval literature would also confirm this assumption: the *Liber colorum* only contains recipes for verdigris whereas malachite is not mentioned. Moreover previous analyses on manuscripts by the French

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illuminator *Maître Boucicaut* indicated that his palette does not include malachite [8]. It was general practice in the late middle ages to add coloured vegetable juices to temper the blueish tonality of verdigris. Such recipes for verdigris could modify the reflectance spectra of the pigment and be at the origin of the broadening of the peak in the absorbance spectra.

Cu and Zn appear to be correlated in the XRF map. We know that a great deal of verdigris was made in the Middle Ages by treating copper in some form with vinegar. In some instances plates of brass have been used, explaining the presence of zinc [16]. More surprisingly K is also found to be co-localized on the XRF map of the green dress of *Dame Fortune*. Looking further into the point analysis, this indicates not only the presence of K but also of Fe and light elements such as Al, Si and Ca. One could interpret this either as the addition of a green earth, to obtain another hue in some zones, or to the presence of lapis lazuli. It is known that lapis can be used either to shadow the greens or as underlayer to give a deep green [8] in medieval illumination. Without any other form of analysis it is difficult to assess which hypothesis should be considered. However zones of different green hues are visible on the macrophotographs but no superposition can be observed, which seems to indicate the use of green earths (Fig. 3b, c).

Text
Vermilion, azurite and gold, easily identified via XRF, are used in the decoration of initials, whereas the black text is likely written with an iron-copper-zinc gall ink as seen in its XRF spectrum. Different inks, iron–copper, iron–zinc or iron–copper–zinc inks have been already identified in French 15th century manuscripts [9]. It would be interesting to investigate whether all folios display the same ink, and to compare the results to other equivalent manuscripts.

Going further to understand the artist's technique
Gold paint or gold leaf?
Gold is widely used in the whole manuscript, sometimes mixed with ochre as in the wheel. In the main illustration, XRF analysis of the frame of the text has shown the presence of gold associated to traces of Cu (about 0.8% according to the semi-quantitative analysis of the spectra), probably as an impurity in the gold ore. It is known that gold can be applied as paint (mixed with a binding medium such as gum Arabic with honey), or in the form of very thin leaves deposited on a preparation layer. In folio 6, observations with the naked eye of the gold areas indicate different appearances and colours: in the border framing the text, above and in the miniature, the gold looks brighter than in the areas of gold in decorative

borders outside of the miniature. The XRF map confirms the presence of different areas of gold corresponding to different application techniques. Outside of the miniature, Ca is co-localized to Au (Fig. 2b). A Ca-rich preparation layer (probably calcite as no sulphur has been detected in this zone) has probably been used to apply gold leaves. In the miniature, this preparation layer cannot be detected; the gold was applied as paint thickly in some parts (the frame of the cartouche and of the miniature) which explain the brighter aspect, or very thinly to enlighten the clothes for example.

It is possible to estimate the gold layer thickness by quantitative XRF as described in the Experimental section. As a first approximation, we consider the thickness of pure gold: the layer of gold can be estimated around 1.5 μm in the frame of the text (painted area) whereas it is approximately 0.1 μm as gold leaf. As an indication, when used for the wheel mixed with iron pigments the gold signals are equivalent to 0.5 μm of pure gold.

Black and brown colours—unusual use of vermilion
Earth pigments have not been—as one might have expected—widely used for the brown colours; an earth colour has been used for example for the shadows of the wheel.

All investigated brown zones, even very dark ones (as the wall behind the king) display high content of lead white and vermilion in the XRF maps (Hg map, Fig. 2). The brown-dark shade must be due to the inclusion in the mixture of an organic black, not detected by XRF. Quantitative analysis can be performed on the different zones displaying vermilion. To compare each zone, the ratio between the Hg-L and Pb-L lines have been calculated: in the brown-dark zones (background, wall, and brown mantle), it lies between 0.05 and 0.1. As a comparison the pinkish hue of Fortune's cheek is obtained with a ratio of 0.008. The wall behind Petrarch indeed shows a slight pink hue, whereas it is not visible at all in the dark background.

It has been highlighted in the literature that browns can be prepared by mixing blacks with reds and yellow pigments [16, 24]: the presence of 'mixed browns' (containing HgS and black pigments) is a feature in Northern European painting at the time as opposed to the earth colours found in Italy.

However other hypotheses can be made to explain such vermilion concentrations, a precious pigment with high tinting power in a very dark background. One may assume that the artist changed his mind and darkened the walls after the addition of vermilion, or that, later on, red or pink walls have been covered. It is also possible that the original red colour has turned into brown or black because of a degradation of the pigment. In the margins,

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vermilion has been used and did not suffer any alteration; however such a difference could be explained by different recipes (other pigments mixed with vermilion in the miniature and/or a different binder). This hypothesis could not be assessed further by means of X-ray fluorescence. The presence of Cl would be an indication of degradation products; however due to the spectral overlap of the Pb–M (around 2.3 keV) and Cl–K (2.62 keV) lines, Cl would be hidden by the large amounts of Pb present in theses zones. Other complementary techniques such as X-ray diffraction or Raman spectroscopy would allow the identification of the Hg- and Pb-based compounds and thus a better understanding of the use of vermilion in brown and dark colours.

Superposition of brazilwood and lapis lazuli to give purple hue

Since Antiquity, purple has been associated with the colour produced by murex [16]. Dyeing molecules extracted from turnsole, called *folium,* corresponded well with the range of ancient purple. Another purple colour enjoyed some importance in medieval painting, a dye from lichen called *orchil* in English [25]. However, except for *folium* and *orchil*, the medieval purple was usually produced with mixtures of red and blue pigments [17, 18, 24]. At the end of chapter 62, Cennino Cennini mentioned that "*if lapis lazuli stone was not so very good, or if you worked the stone up so much that the blue did not come out violet [...] take a bit of punded kermes and a little brazil, cook them together*".

In our case, no characteristic chemical element is seen in the XRF maps. According to the reflection spectrum (Fig. 5), it can be either a violet dye (such as elderberry) [19, 26] or the superimposition/mixture of a red dye and the blue lapis-lazuli pigment. Macro-photographs clearly confirm the second hypothesis: a blue pigment (likely lapis lazuli) has been applied over a red layer to give the purple tint (Fig. 5).

Simulations of both XRF and reflectance spectra have been performed to assess whether they could have been used to discriminate the origin of the violet colour.

The XRF spectrum can be simulated as a superimposition of brazilwood and lapis over lead white (with an effective uniform lapis thickness about 0.7 μm, on top of
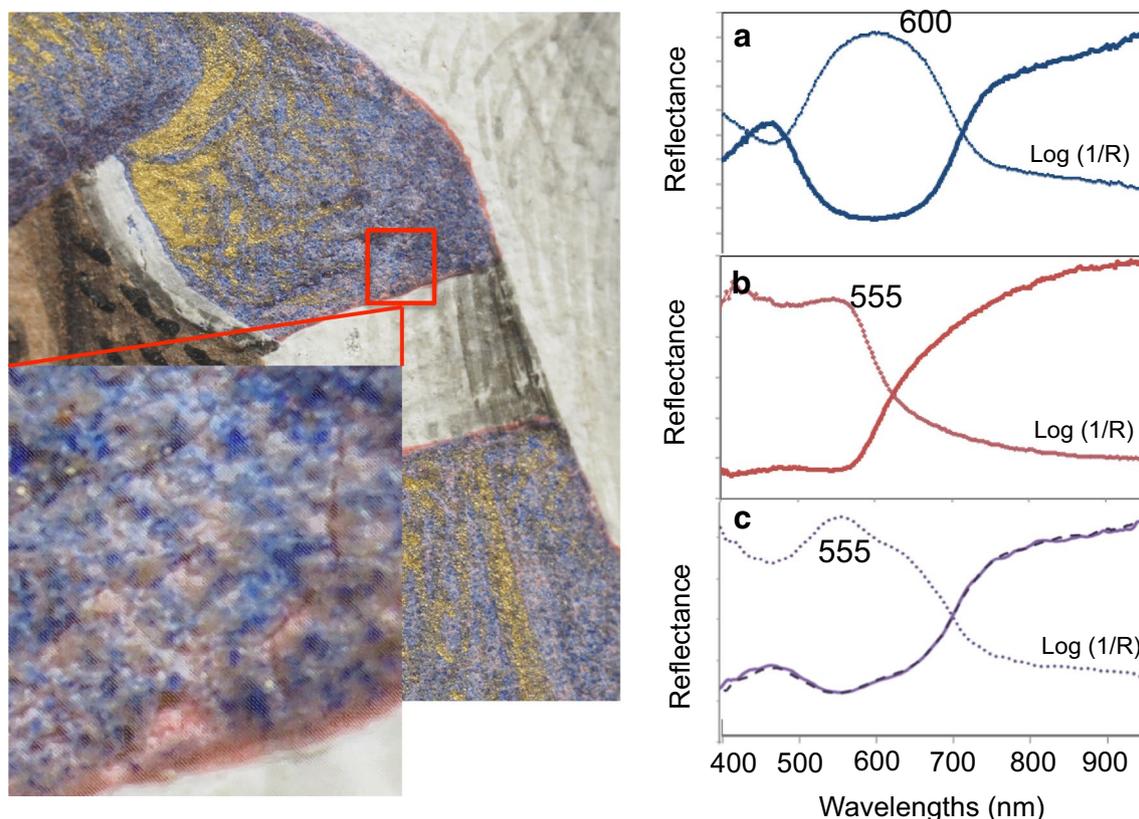
Fig. 5 (Left) Macro-photograph of purple dress of the woman in the foreground, (Right) reflectance spectra of **a** the blue dress of Fortune (lapis-lazuli), **b** the red mantle of Pretrarch (brazilwood) and **c** the purple dress—straight line—and the Kubelka–Munk simulation—dash line—for 42% of brazilwood and 58% of lapis

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a 0.9 μm layer of brazilwood, applied over a 5 μm lead white layer) or as a mixture of brazilwood and lapis over lead white. There are different reasons for this: the layers are very thin and composed of light elements. Moreover, careful observation of the macrophotograph indicates that this is not an instance of superimposed transparent glazes: the red colour is visible in between the large particles of lapis. The purple hue is thus obtained not only by the superimposition of transparent blue and red glaze layers, but also by the juxtaposition of both colours.

The reflectance spectrum of the purple colour has also been simulated. It is known that the reflectance spectrum of a paint mixture is not simply the linear combination of the components' spectra. Radiative transfer equations or their approximation, the so-called single constant Kubelka–Munk (KM) theory, have to be considered to successfully describe the light transport in the turbid system of paint mixtures. Liang et al. [27] recalls the principle of the KM theory, the main assumptions and its limitations. In the KM theory the diffuse reflectance (R) of an infinite optical thickness layer is described by:

$$\frac{K}{S} = \frac{(1-R)^2}{2R}, \text{ and inversely: } R = 1 + \frac{K}{S} - \sqrt{\left(\frac{K}{S}\right)^2 + 2\frac{K}{S}},$$

with K the effective absorption and S effective scattering coefficients.

In simple cases (taking into account diffuse illumination and collection), the K and S coefficient of paint mixtures are linear combinations of the paint components weighted by their concentrations. This description works well for pigment mixtures and transparent, superimposed layers [28]. A perfect match of the model with the experimental data was obtained between the theory and the experimental curve for 42% of brazilwood and 58% of lapis (Fig. 5). For this calculation we used the spectra recorded on the manuscript, both layers are applied on highly scattering white paint. While this allows for a qualitative correct recording of the reflectance curve, it does not allow for a precise quantitative one, rendering the results semi-quantitative.

As a conclusion, based on the observations of the purple zones in macrophotographs, their XRF spectra can be simulated as well as their reflectance spectra: both methods indicate close proportions of brazilwood lake and lapis lazuli. The desired hue can then be modulated by variations of their proportions. This illustrates the value of macro-photographs as they allow one to interpret the spectra recorded, that take an average of an area much larger than the lapis particles.

Shadows and light

Specific attention can be devoted to the way shadows and light are executed in the miniature. It is particularly striking that even in some tiny details, light and shadows have been applied as very thin layers. This is shown for the red fruit in Fig. 4: on the vermilion where gold paint has been applied on the left as a highlight, and on the right a thin glaze of brazil-wood was used to create an initial degree of shadow. A fourth pigment has been used, carbon black, for a darker shadow to model the hole in the fruit. On the characters' clothes such precise detailed work is also observed: a thin layer of the iron–copper–zink ink, the same as used for the text, is used for the shadows (as revealed by the comparison of light/dark zones on the blue dress of Fortune). It is difficult to state whether the ink has also been used to model shadows on the faces as the X-ray beam size does not allow us to resolve such tiny details; however the macrophotographs reveal the same type of hatching on the faces and on the clothes which would indicate that the same material was used (Fig. 3d).

Clear zones are obtained with gold paint applied onto the coloured layer. This observation could also be made for the work of *Maître Boucicaut* by Guineau et al. [8]. They point out that each colour is associated to a shadow and highlight. French artists such as the master of Boucicaut and the author of our manuscript used gold and shadows with thin ridges or glazes. This refinement in modelling objects and characters, but also in the composition and the three-dimensional representation of the scene can be underlined and put in the perspective of early Renaissance panel paintings [24].

Revealing the hidden coat-of-arms: a new clue in the attribution of the manuscript

The coat-of-arms at the bottom of the rich illumination of folio 6 has been covered with red paint. By transparency, on the reverse side of the folio, we can distinguish with the naked eye an alternation of red and dark bands and some elements that may suggest a border.

Results of XRF mapping in reconstructed elemental maps of specific elements of the coat-of-arms are shown in Fig. 6. The XRF maps indicates the use of red (vermilion HgS), identified through the Hg-L X-line emission and reveals three gold bands painted on a red background.

Moreover, both spatial distribution of mercury and gold in the coat-of-arms reveals the fact, not visible with naked eye, that the border is divided into compartments of reversed colors to the main pattern of the coat-of-arms. The blazon would therefore correspond to the reconstructed drawing presented in Fig. 7.

In heraldry, this coat-of-arms is described as *fascia of gold and gules of six pieces, with the counterfasted border of the one in the other*. These arms are those of Tanguy IV du Châtel Viscount de la Belliere (who died in 1477). He served at Louis XI's court. Is the presence of Tanguy IV du Châtel's coat-of-arms, a new step in the attribution

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Fig. 6 Hidden coat-of-arms observed on folio 6 of Petrarch held in Méjanes library in Aix-en-Provence (top, left) and the corresponding XRF mapping
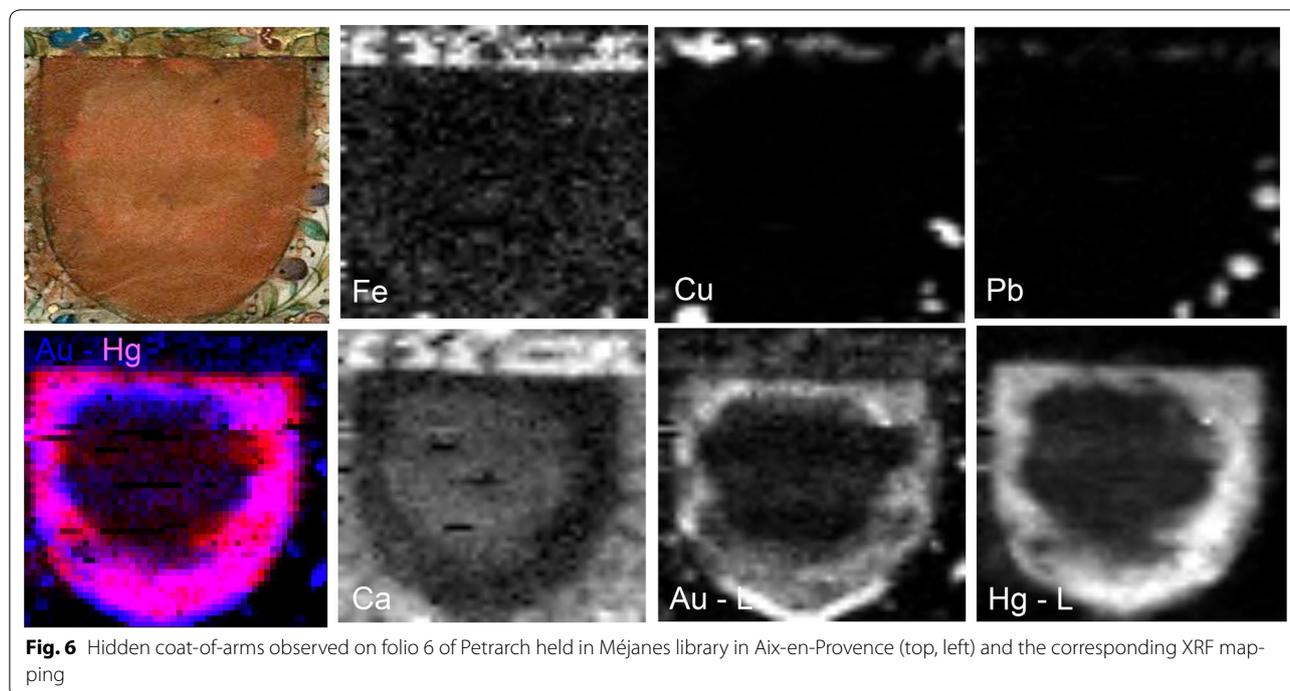
of the manuscript held in Aix-en-Provence? In order to answer to this question, it is important to note that his coat-of-arms is also found on the manuscript *De remediis utriusque fortunae* held in the National Library of Vienna (Fig. 7). It is, in this case, associated with his wife's crest. We know that this latter manuscript has been illuminated by François Le Barbier for Jacques d'Armagnac who participated in several revolts against Louis XI and was arrested in 1476 after the siege of his castle by Pierre de Beaujeu, Jean du Mas and Tanguy IV du Châtel. They shared between them the rich library created by Jacques d'Armagnac. Tanguy IV du Châtel decided to add his coat-of-arms (and his wife's) on the manuscripts he kept, ordering that it should be painted over those of Jacques d'Armagnac.

The identification of the coat-of-arms is a key element supporting an hypothesis of attribution of the decoration of this manuscript to the workshop of François Le Barbier: what we know of the library of Tanguy IV du Châtel show that he was a very regular client of this workshop.

Conclusion

Macrophotography, MA-XRF scanning and visible hyperspectral reflectance imaging have been combined with point analysis with quantitative data treatment to reconstruct the palette employed and answer specific questions regarding the techniques and materials used. It was then possible to go further in the recovery of the history of the manuscript under investigation.

We have focused our investigations on mixtures and superimposed colours, which have not been studied to the same extent in the literature. Specific materials have been identified in the miniature, more precious than the ones used in the surrounding decorative motifs. The way shadows and light are created, but also the use of brazilwood lakes can be underlined and put in relation with the practice of French illuminators. More specific features could also be highlighted such as the specific use of vermilion in the dark colours. The exact nature of the purple colour could also be identified as the result of the superimposition of a blue lapis layer with large grains on a red brazilwood lake underlayer.

These results can be used as a basis for an in-depth comparison of the palette and the techniques used by François Le Barbier's workshop for well-identified manuscripts contributing to a more precise knowledge of Parisian workshop practice in the 15th century. Moreover, the refinement and delicacy of the miniature underlined through our analyses, reveal illuminators as true artists. Illuminated, manuscripts can be considered as galleries of paintings, kept in better conditions than any other artwork from the Middle Ages, and deserve

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Fig. 7 Left: Petrarch, Les *remèdes de l'une et l'autre fortune* (Folio 5v), National Library in Vienna (Austria), with a zoom on the Coat-of-arms (right, down). On the right (top): Reconstructed drawing of the coat-of-arms

in-depth investigations of their materiality, to the same degree as easel paintings.

Authors' contributions
LV, SR, FB collected the reflectance and fluorescence imaging spectroscopy data and completed the data treatment and interpretation. MA helped in the data treatment, PW, SA and VG helped in their interpretation. The manuscript was written by LV and edited by LV, SR and MA. All authors read and approved the final manuscript.

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