

# Forgery detection on an Arabic illuminated manuscript by micro-Raman and X-ray fluorescence spectroscopy

A. Duran,<sup>a,b\*</sup> M. L. Franquelo,<sup>a</sup> M. A. Centeno,<sup>a</sup> T. Espejo<sup>c</sup>  
and J. L. Perez-Rodriguez<sup>a</sup>



An Arabic manuscript, supposed to be from the 14th century, was investigated and its components (pigments and dyestuffs) characterised using micro-Raman and X-ray fluorescence (XRF) spectroscopy, the latter employing a portable XRF/X-ray diffraction (XRD) system. The presence of anatase, rutile, calcite, barite, zinc oxide, carbon black, vermilion, hematite, goethite,  $\beta$ -naphthol, copper phthalocyanine, pigmosol green and a brass-based pigment was detected in the different zones of the illuminated manuscript. The detection of titanium oxides, barite and organic synthetic colourants such as  $\beta$ -naphthol and copper phthalocyanine and derived compounds provides indisputable indication of forging, repainting or retouching after the 19th century in the image of the manuscript. Copyright © 2010 John Wiley & Sons, Ltd.

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**Keywords:** micro-Raman; XRF/XRD portable system; forgery; dyestuffs; Arabic illuminated manuscript

## Introduction

An illuminated manuscript is one in which the text is complemented by the addition of borders, decorated initials or miniature illustrations. Every manuscript bears witness to the culture from which it originated. In this sense, the heritage left by Arabs is directly related to their documentary sources in the different historical periods.

Artwork on paper supports is very delicate compared to other types of artwork. Removal of even small fragments of the artwork is not usually possible, and new strategies of analysis based on only strictly non-invasive techniques are required for the complete characterisation of their components (support, binders, pigments and dyestuffs).<sup>[1,2]</sup>

Micro-Raman spectroscopy has become a very useful tool for the analysis of artwork on paper because of its reproducibility and sensitivity, associated with the non-destructivity and rapidity, and also because of the reasonably low cost compared to other techniques.<sup>[1,3]</sup> Several reports have been published in relation to the application of micro-Raman spectroscopy to the analysis of artwork on paper (manuscripts, bibles, maps, wallpapers, poetry books or stamps).<sup>[1–11]</sup> Nevertheless, it is sometimes found that some pigments fail to give an identifiable Raman spectrum either because they are poor Raman scatterers or because of fluorescence of the binding medium or of the colouring matter itself, while others do not even produce a detectable Raman signal.<sup>[12]</sup> It may therefore be necessary to complement the micro-Raman technique with other analytical techniques in order to characterise thoroughly the palette used.

Micro-X-ray fluorescence ( $\mu$ -XRF) is the microscopic equivalent of bulk XRF and it is a suitable analytical method for the analysis of cultural objects; apart from its non-destructive character,  $\mu$ -XRF is a fast, accurate, sensitive, universal, versatile and multi-elemental analytical method.<sup>[13–15]</sup> Most recently, the need to perform *in situ*

non-invasive analysis of artwork that cannot be removed easily from their locations has led to the development of portable XRF spectrometers. An XRF portable system has been recently designed and constructed in the laboratory of the Centre de Recherche et de Restauration des Musées de France (C2RMF), which combines XRF and X-ray diffraction (XRD) in the same apparatus.<sup>[15–18]</sup>

In the present study, an Arabic manuscript, supposedly from the 14th century, was investigated and its components (mainly pigments and dyestuffs) characterised. Recently, we have reported on the characterisation of the materials forming part of this manuscript employing mainly XRD with micro-XRD and portable equipment,<sup>[17]</sup> but in this paper we focus our attention on the performance of micro-Raman and XRF experiments. Results by XRD will be compared with those provided by micro-Raman and XRF in the conclusion.

## Experimental

The dispersive integrated Horiba Jobin-Yvon LabRam HR800 system was employed for recording the Raman spectra. The

\* Correspondence to: A. Duran, Materials Science Institute of Seville, Avda Americo Vesputio 49, 41092 Seville, Spain. E-mail: adrian@icmse.csic.es

a Materials Science Institute of Seville, Avda Americo Vesputio 49, 41092 Seville, Spain

b Centre de Recherche et de Restauration des Musées de France, 14 quai François Mitterrand, 75001 Paris, France

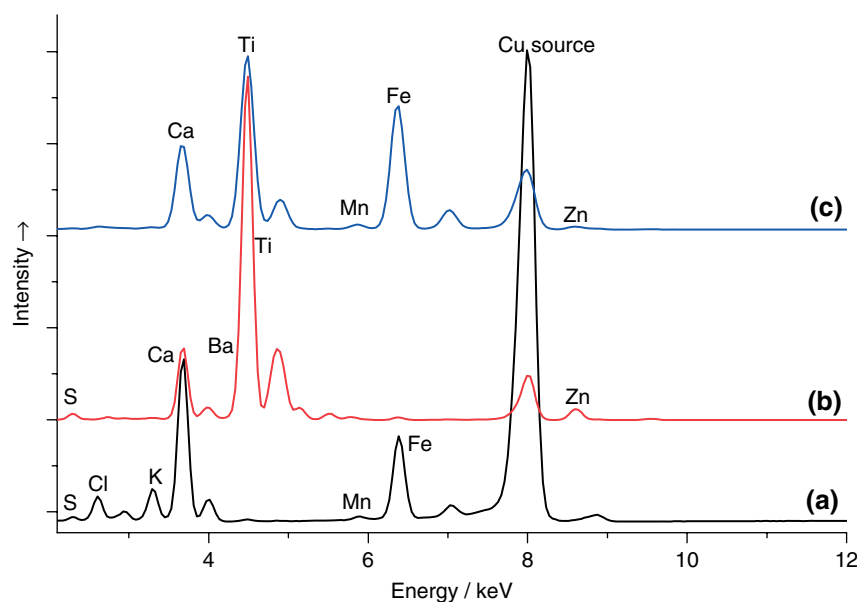
c Painting Department of Fine Arts Faculty, University of Granada, Avda Andalucía, s/n, 18071 Granada, Spain



**Figure 1.** Photographs: (a) micro-Raman system setup; (b) XRD/XRF portable system setup; (c–h) illuminated manuscript showing the measurement zones (and magnifications, e–h).

experiments were performed directly on the manuscript as shown in Fig. 1(a). Two external visible diode lasers (solid-state source) are available in this apparatus: at 532.1 nm (green) and at 784.6 nm (red), but we have mainly used 784 nm to minimise fluorescence of the organic medium or of the pigments/dyestuffs themselves. The equipment has a charge-coupled device (CCD) detector and a grating of 600 grooves/mm. An optical microscope is coupled confocally to the Raman spectrometer. Almost all the measurements shown in this paper have been collected at 50 $\times$  and 100 $\times$  magnifications. The size of most of the analysed zones is approximately of 25  $\mu\text{m}^2$ . Each Raman spectrum was recorded for 8–12 min and with a spectral resolution of 2  $\text{cm}^{-1}$ . The laser power ranged from 16 to 40 mW to avoid any damage to the manuscript, which is very delicate.

The interpretation of the Raman spectra usually requires some knowledge of the materials under study, in this case, the illuminated manuscript. XRF is being currently used for elemental identification and, when associated with XRD, is very effective for the characterisation of materials and complements the information provided by micro-Raman spectroscopy. The XRD/XRF portable system used is profusely explained in Refs [15–19]. We employed an X-ray tube (40 kV, 700  $\mu\text{A}$ ) with a copper anode; the XRF detector was a silicon drift detector (Röntec GmbH) with an active area of 5  $\text{mm}^2$  and full width at half-maximum (FWHM) of 150 eV at 5.9 keV. It was Peltier-cooled to  $-10^\circ\text{C}$  and was located at  $90^\circ$  to the X-ray tube and on the axis normal to the analysed sample surface. At the exit of the tube, we used a slit of 0.5 mm; therefore the measured area was around 9  $\text{mm}^2$  (Fig. 1(b)). An Al



**Figure 2.** XRF spectra of (a) background (paper); (b) white zone of the image; (c) black zone of the image.

filter was used at the exit of the tube for detecting the presence of copper in the blue and green zones. XRD data were collected with imaging plates as a 2D detector.

Figure 1(c–h) shows the different zones measured on the manuscript. The analysed manuscript forms part of the book *Lubab al-Ta'wilfi ma'ani al-tanzil*, written by Al-Jazin (d. 725 H/1324 EC) in the 14th century. The dimensions of the manuscript are 295 mm long and 220 mm wide (Fig. 1(c) and (d)). It contains a woman's scene represented in the *hamman*, which is completed with two written lines at the top and three at the bottom of the folio (Fig. 1(c)). On the other side of the manuscript, comments of some *aleyas* of the *azora* of the bee can be seen (Fig. 1(d)).

## Results and Discussion

### Background

XRF spectra were collected from a zone of the manuscript where colour is absent (labelled as paper) (Fig. 1(d) and (f)) showing the presence of calcium (Fig. 2(a)). Raman analyses did not reveal the presence of calcium carbonate or calcium sulfate because of problems of fluorescence. The use of calcium sulfates should be ruled out taking into account that the molar ratio Ca/S was different from 1 : 1 (Fig. 2(a)). The most likely reason would be the presence of calcium carbonate, produced from the carbonation of lime, which is usually employed in parchment manufacture.<sup>[6,9]</sup>

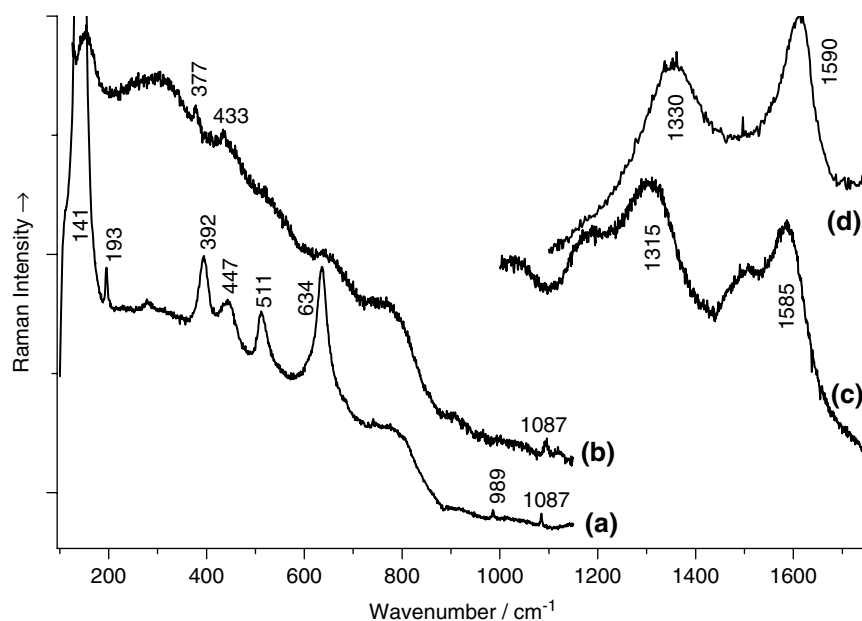
A common observation in all the coloured zones studied by XRF was the presence of calcium, titanium and zinc, and also barium in almost all cases. Elemental analysis by the XRF technique is difficult in the case of illuminated manuscripts, which comprise a superimposition of coloured layers on a paper support. Data from more than one layer or even from the other side of the manuscript can be recorded in the same spectrum, so the interpretation is not easy.<sup>[11]</sup> These problems could be overcome by using a combination of XRD techniques in transmission and reflection modes.<sup>[17]</sup>

### White pigments

The presence of calcium, barium, titanium and zinc was detected by XRF (Fig. 2(b)) in zones of white (Fig. 1(c) and (g)). Some difficulties appear when trying to distinguish between titanium and barium by XRF in samples containing both elements, due to the overlapping of the lines of emission of both elements: lines  $K\alpha = 4.51$  keV of Ti and  $L\alpha = 4.46$  keV of Ba; and  $K\beta = 4.93$  keV of Ti and  $L\beta = 4.83$  keV of Ba. But the distinction was made possible by searching for other lines of lower intensity, such as  $L\gamma = 5.53$  keV of Ba, which are not usually easily distinguishable. Calcium carbonate ( $\text{CaCO}_3$ , mineral calcite) was identified in these zones, based on the observation of the characteristic sharp Raman band at  $1087\text{ cm}^{-1}$ <sup>[7,20,21]</sup> (Fig. 3(a) and (b)). Titanium dioxide ( $\text{TiO}_2$ , anatase) and barium sulfate ( $\text{BaSO}_4$ , barite) were also detected by the presence of their main Raman bands at 141, 193, 392, 447, 511 and  $634\text{ cm}^{-1}$ <sup>[22]</sup> and at  $989\text{ cm}^{-1}$ ,<sup>[23]</sup> respectively (Fig. 3(a)).

Titanium dioxide ( $\text{TiO}_2$ , rutile) and zinc oxide ( $\text{ZnO}$ ) were also identified in another white zone (not far from the previous one), together with the compounds mentioned before. Zinc white is a particularly difficult pigment to detect by Raman spectroscopy as it is highly fluorescent,<sup>[24]</sup> but in our case it was possible thanks to its Raman bands at 433 and  $377\text{ cm}^{-1}$  (Fig. 3(b)). Variable amounts of zinc were found by XRF in most areas, suggesting that zinc white is present as a filler/extender or as a component in pigment mixtures.

Calcium carbonate must be seen as an extender and/or filler of the other pigments. Natural barium sulfate was introduced as an artists' material in 1782 but it was not used extensively until the introduction of synthetic barium sulfate in 1810–1820. The presence of barium sulfate has been related to the presence of synthetic organic pigments in some of the most modern samples as well as an extender.<sup>[11]</sup> Zinc white (zinc oxide) and titanium white (titanium dioxides, rutile and anatase) replaced lead white (cerussite and hydrocerussite) in artworks at the beginning of the 20th century.<sup>[1,25]</sup> Taking into account these data, the presence of these compounds in the illuminated manuscript studied provides indisputable evidence for restoration/retouching or forgery.



**Figure 3.** Micro-Raman spectra collected on (a) white zone of the image; (b) other white zone of the image; (c) black letter; (d) black zone of the image.

## Black pigments

### Black letters

The study of the black letters of the manuscript was performed on the text positioned on top of the image (Fig. 1(c) and (e)). No characteristic chemical elements were found in the black letters by XRF. The XRF spectrum is similar to that collected from the paper (Fig. 2(a)). Light elements are not usually detected by our equipment because of the strong absorption in the Be window and in the air (2–3 cm) between the samples and the XRF detector; X-ray transmission in air is about 5% for 3 cm and 40% for 1 cm at the Si K energy (1.74 keV).<sup>[15,16]</sup> In this form, light elements such as phosphorus or carbon are not detected. The detection limits for light elements could be improved by reducing the distance between the sample and the detector or replacing air by helium.<sup>[15]</sup> The micro-Raman study of black letters showed curves typical of carbon black, with bands at 1315 and 1585  $\text{cm}^{-1}$  (Fig. 3(c)).

### Black zones of the image

XRF study performed on the black areas of the image (Fig. 1(c) and (h)) did not show the characteristic chemical element responsible for the colour in these zones (Fig. 2(c)). However, micro-Raman spectra collected from these zones showed clearly the presence of carbon-based black, identified by the characteristic broad Raman bands centred near 1330 and 1590  $\text{cm}^{-1}$  (Fig. 3(d)). The shape of Raman peaks is consistent with that of an amorphous carbon-based black pigment.

Carbon black is the name of a common black pigment, traditionally produced from charring wood; it consists of pure elemental carbon.

## Red, orange and brown pigments

### Red letters

This experiment was carried out on the reverse side of the manuscript (Fig. 1(d) and (f)). The XRF spectrum of the red letters

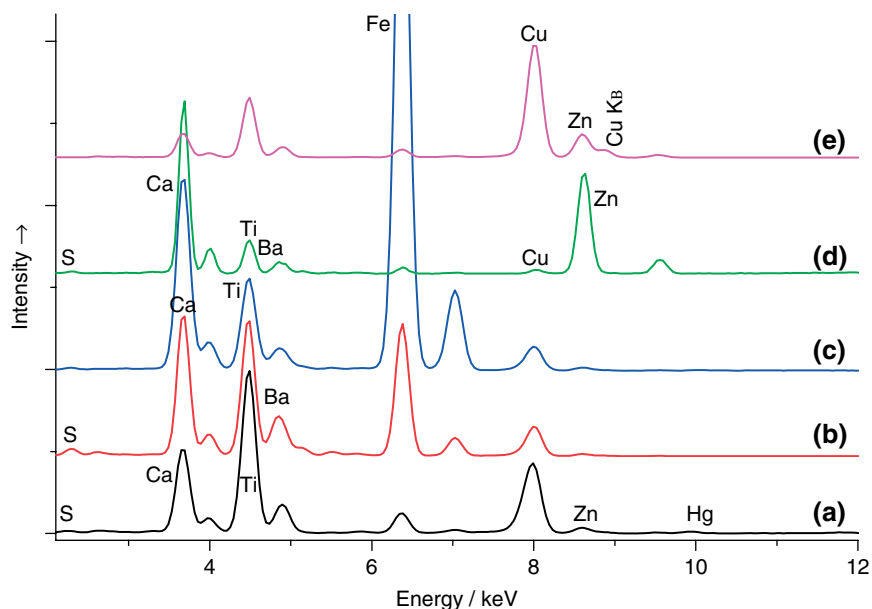
shows mercury and sulfur peaks, two elements that can be related to the red pigment vermilion ( $\text{HgS}$ ) (Fig. 4(a)), and also those corresponding to titanium, zinc and barium. Bands at 254  $\text{cm}^{-1}$  (typical of the  $\text{Hg-S}$  stretching vibrations)<sup>[2]</sup> and 343  $\text{cm}^{-1}$  were detected (Fig. 5(a)) by micro-Raman spectroscopy. Vermilion is very easy to detect by Raman spectroscopy, as  $\text{HgS}$  has a very large scattering cross-section when excited in the red or infrared.<sup>[7,20]</sup>

This mercury sulfide is a red pigment that was frequently used by artists from antiquity until the 20th century. This pigment was traditionally employed on medieval manuscripts.<sup>[24]</sup> Both vermilion from mining sources (also called cinnabar) and from artificial production were used; however, neither XRF nor Raman spectroscopy allows making a distinction between the natural and synthetic variants.<sup>[21]</sup>

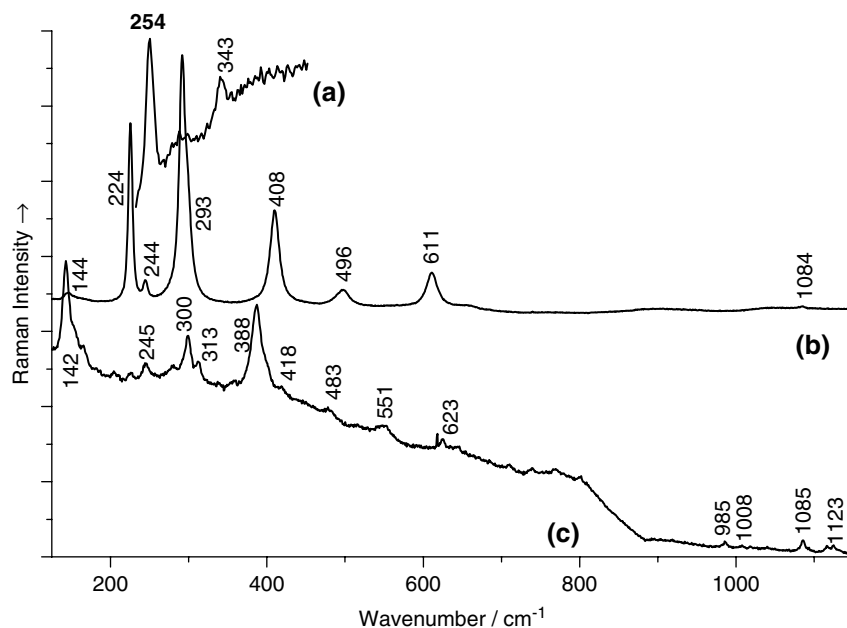
Titanium, zinc and barium were detected by XRF in the red and also in the black letters (not labelled, Fig. 1(d) and (f)) written on the reverse of the manuscript, but these elements were not detected by XRF in the black letters on top of the image in the obverse side of the manuscript (Fig. 1(c) and (e)). The measured zones on the reverse (red and black letters, Fig. 1(d) and (f)) coincide with coloured zones of the image on the other side of the manuscript (Fig. 1(c)); in this way, Ti, Zn and Ba collected in the XRF spectra of the red and black letters could come from a coloured layer of the image on the other side because of the large penetration of X-rays.

### Reddish zones (red, orange and brown) of the image

A modern synthetic red colourant has been detected in some red and brown zones (Fig. 1(c), (g) and (h)) thanks to micro-Raman spectroscopy. Figure 6(a) and (b) shows the experimental spectrum collected from a red zone, and Table S1 (Supporting Information) gives the theoretical Raman data of the standard  $\beta$ -naphthol (monoazopigment).<sup>[26]</sup> The experimental bands (at 313, 513, 593, 623, 709, 737, 768, 892, 1039, 1092, 1123, 1155, 1188, 1224, 1238, 1266, 1288, 1336, 1395, 1451, 1485, 1554 and 1586  $\text{cm}^{-1}$ ) match very well with those from the standard, and therefore we can definitely conclude the presence of this compound.



**Figure 4.** XRF spectra of (a) red letter; (b) red zone of the image; (c) orange zone of the image; (d) blue zone of the image (with Al 750- $\mu\text{m}$  filter); (e) golden area of the image.



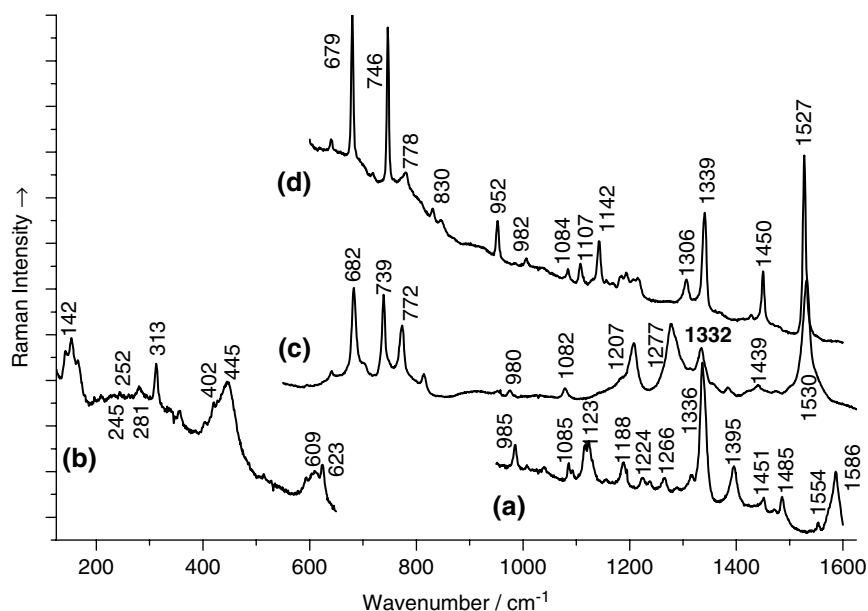
**Figure 5.** Micro-Raman spectra of (a) red letter; (b) brown zone of the image; (c) orange zone of the image.

Also, bands corresponding to anatase ( $142\text{ cm}^{-1}$ ), rutile ( $245$ ,  $445$  and  $609\text{ cm}^{-1}$ ), calcite ( $1085\text{ cm}^{-1}$ ), barite ( $985\text{ cm}^{-1}$ ), vermilion ( $252\text{ cm}^{-1}$ ) and hematite ( $281$  and  $402\text{ cm}^{-1}$ )<sup>[20,22,23]</sup> (Fig. 6(a) and (b)) were detected in the spectra collected on the red areas. XRF spectra collected from these areas showed the presence of high amounts of calcium, barium, titanium, iron and also a small quantity of zinc and mercury (Fig. 4(b)).

The identification of organic synthetic red colourants in manuscripts, where sampling is not usually an option, is a continuous challenge, and work is being undertaken to explore different options, such as longer wavelength excitation or surface-enhanced Raman spectroscopy.<sup>[7]</sup> A relatively small group of azo-pigments, which are among the oldest synthetic organic

pigments, provides primarily red and a few orange hues.  $\beta$ -Naphthol pigments provide colours in the range from orange to medium red. The typical coupling reaction with  $\beta$ -naphthol as a coupling component yields such well-known pigments as toluidine and dinitroaniline orange. The first azo-pigments were produced around 1870, and only a few of these are still used today, primarily for inexpensive applications, because the pigments are cheap to manufacture and only moderately lightfast.<sup>[26,27]</sup>

Similar XRF spectra (Fig. 4(c)) were collected from the brown and orange zones of the manuscript (Fig. 1(c) and (g)). Iron is present in very high quantities (even piles-up are visible in spectra at 12.8 and 14 keV). Hematite ( $\text{Fe}_2\text{O}_3$ ) was clearly identified in the brown zones thanks to its distinctive Raman spectrum (Fig. 5(b)) with bands



**Figure 6.** Micro-Raman spectra collected on (a) red zone of the image (range 950–1600  $\text{cm}^{-1}$ ); (b) red zone of the image (range 125–650  $\text{cm}^{-1}$ ); (c) green zone of the image; (d) blue zone of the image.

at 224, 244, 293, 408, 496 and 611  $\text{cm}^{-1}$ .<sup>[20,23]</sup> The broadening of the peak at 611  $\text{cm}^{-1}$  and the wavenumber shift to higher values could be explained by the presence of magnetite mixed with hematite.<sup>[28]</sup> Calcite (1084  $\text{cm}^{-1}$ ) and anatase (144  $\text{cm}^{-1}$ ) were also detected by micro-Raman spectroscopy. The Raman spectrum collected from an orange zone showed the presence of bands at 245, 300, 388, 418, 483, 551 and 1008  $\text{cm}^{-1}$ , attributed to goethite ( $\text{FeOOH}$ )<sup>[20,22,23]</sup> and also those corresponding to anatase (142  $\text{cm}^{-1}$ ), calcite (1085  $\text{cm}^{-1}$ ) and barite (985  $\text{cm}^{-1}$ ) as well as of the modern dyestuff detected previously in the red zones ( $\beta$ -naphthol azo-pigment) (313, 623, 1123  $\text{cm}^{-1}$ ) (Fig. 5(c)).

Regarding the iron compounds detected, hematite and goethite are very abundant natural materials, and it is not unusual to detect them on a medieval work of art.<sup>[24]</sup> Goethite is the chromophore of all yellow natural pigments, and hematite that of the red ones.<sup>[28]</sup>

### Green and blue synthetic organic pigments

Copper (Fig. 4(d)) was detected in the green and blue coloured zones (Fig. 1(c), (g) and (h)) by XRF. The use of a copper source is not usual for micro-XRF portable systems since copper fluorescence lines are always present in the spectra collected, preventing the detection of copper in the artwork studied.<sup>[16]</sup> We have used a 750- $\mu\text{m}$  Al filter placed at the exit of the X-ray tube, which allows absorption of all X-rays up to copper emission lines from the tube. In this form, the copper K photons collected come only from the fluorescence signal of the sample analysed.<sup>[16]</sup> Fig. 4(d) shows the spectra collected on a blue zone using the Al filter.

Zones of both colours (green and blue) were complicated to measure by micro-Raman spectroscopy because of the high fluorescence. Several previous works have reported difficulty in clearly identifying certain green pigments due to the weakness of Raman bands and fluorescence masking effects.<sup>[29]</sup> However, the Raman spectrum collected on an area of this colour showed strong characteristic bands at 682, 739, 772, 1207, 1277, 1332, 1439 and 1530  $\text{cm}^{-1}$  (Fig. 6(c)), which match the Raman spectral features of chlorinated copper phthalocyanine (Table S1). Similarly, copper

phthalocyanine (bands at 679, 746, 778, 830, 952, 1107, 1142, 1306, 1339, 1450 and 1527  $\text{cm}^{-1}$ ) (Fig. 6(d)) was detected in blue areas (Table S1). In these zones, rutile, calcite (1082, 1084  $\text{cm}^{-1}$ ), anatase and barite (980, 982  $\text{cm}^{-1}$ ) were also detected, but only a part of the experimental spectrum is shown in Fig. 6(c) and (d).<sup>[22,27]</sup>

Until mid-18th century, the materials forming part of the artwork corresponded to pigments known since antiquity, even though by that time others had already been artificially synthesised and were available.<sup>[1]</sup> By the end of the 19th century, synthetic organic pigments were gradually introduced into the market and started to replace inorganic pigments as artists' pigments, such as lithographic inks, where their main advantage was that they had hues not accessible with inorganic pigments alone.<sup>[30]</sup> Their industrial manufacture has always been a by-product of the dyestuff industry.<sup>[27]</sup> Copper phthalocyanine (also called blue phthalocyanine) was first synthesised in 1935. It is a bright, greenish-blue crystalline synthetic blue pigment, frequently used in paints and dyes, with high covering power and resistance to the effects of alkalis and acids.<sup>[29–31]</sup> The chlorinated copper phthalocyanine (also called pigmosol green and phthalocyanine green) is a phthalocyanine blue in which most of the hydrogen atoms are replaced with chlorine. It has a bright, high-intensity green colour.<sup>[29,31]</sup>

The presence of synthetic organic colourants such as phthalocyanines blue and green and  $\beta$ -naphthol (azo-pigment), used in dyestuffs, is an indisputable indication that the manuscript was retouched after 19th century.

### Brass pigments

The detection of compounds responsible for the golden areas (Fig. 1(c) and (g)) was not easy. XRF spectra collected on these zones did not show the characteristic chemical elements. A noticeable amount of zinc and copper was detected (Fig. 4(e)), but both elements are present in all the coloured zones studied by XRF. Zinc oxide is possibly present in almost all the areas; copper fluorescence lines always appear because of the use of a source of

copper, although in this case the line Cu K $\beta$  is clearly visible showing the definite presence of this element in this area.<sup>[16]</sup> Experiments using the Al filter also show the presence of copper. The presence of elements such as copper and zinc or alloys containing both could not be directly ascertained by Raman spectroscopy.

The determination was possible by XRD, which was performed with the XRD/XRF portable system at the same time as the XRF measurements. Diffraction peaks at  $2\Theta = 42.5^\circ$  and  $49.5^\circ$  were observed and assigned to brass (copper–zinc alloy).

The use of brass to make the colourant is not very common and rarely documented. The use of a brass ink can be justified by the fact that a copper–zinc alloy poor in zinc (between 10 and 18%) shows a pleasing golden yellow colour and is a cheaper alternative to gold.<sup>[6]</sup> A few examples of the use of brass-like pigment can be seen in medieval manuscripts.<sup>[6,32,33]</sup>

## Conclusions

An Arabic illuminated manuscript was studied by means of micro-Raman and XRF. The palette used to illuminate the artwork and to write the text was completely characterised.

The materials identified in the text (letters) were the following: vermilion, carbon black and possibly calcite. In the different coloured zones of the image, we have observed the presence of anatase, rutile, calcite, barite and zinc oxide employed as white pigment and/or extenders and fillers; carbon black as black pigment; hematite and goethite as reddish pigments and  $\beta$ -naphthol as colourant forming part of the red dyestuff; phthalocyanine-derived compounds as organic colourants of the blue and green dyestuffs; and, finally, a brass-based pigment in the golden area.

The detection of titanium oxides (anatase and rutile), barite and organic synthetic colourants such as  $\beta$ -naphthol or copper phthalocyanine and derived compounds only in the image provides an indisputable indication of forgery, repainting or retouching after the 19th century in some zones of the manuscript. However, the written text (letters) could be original (from the 14th century). The analyses we have conducted and presented in this paper lead us to declare that the images were possibly copied from another document recently, reusing an old written folio, to sell it as an original souvenir later.

The combination of the molecular information provided by micro-Raman spectroscopy and the elemental information obtained by means of XRF gives a complete overview of the compounds present on the studied artwork.

Table S2 shows the list of compounds detected by the XRD systems (experiments performed in transmission –  $\mu$ -XRD – and reflection – XRD portable – modes)<sup>[17]</sup> and those by micro-Raman spectroscopy and XRF. The organic synthetic colourants and the black pigments were detected only by Raman spectroscopy, and the brass-based pigment only by XRD. The identification of the rest of compounds was possible by employing both techniques; the coincidence in the other results was almost total as shown in Table S2. The combination of the different XRD procedures allowed definite conclusions to be drawn on the layer distribution of the materials in the manuscript.<sup>[17]</sup>

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## Supporting information

Supporting information may be found in the online version of this article.

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