"MICRO-RAMAN AND XRF SPECTROSCOPY AS NON-DESTRUCTIVE TECHNIQUES FOR PIGMENTS AND DYESTUFFS IDENTIFICATION IN AN ARABIC ILLUMINATED MANUSCRIPT"

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INTRODUCTION AND AIM OF THE WORK:

An illuminated manuscript is a manuscript in which the text is complemented by the addition of borders, decorated initials or miniature illustrations. Every manuscript bears witness to the culture in which it was originated. In this sense, the heritage left by Arabs is directly related to their documentary sources in the different historical periods. In the study presented here, an Arabic manuscript, supposed from the 14th century was investigated and the characterisation of its components (mainly pigments and dyestuffs) performed.

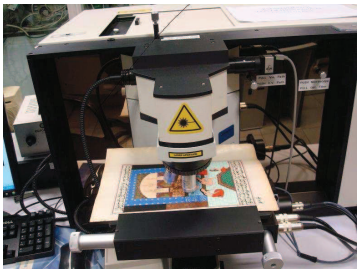

Figure 1.- Experimental set-up of the micro-Raman system employed for manuscript analysis. Materials Science Institute of Seville.

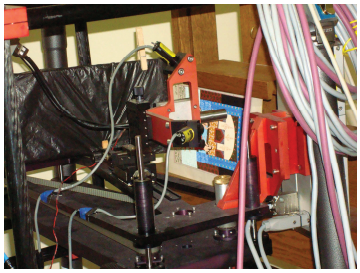

Figure 2.- Experimental set-up of the XRD/XRF portable system employed for manuscript analysis. Centre de Recherche et de Restauration des Musées de France.

EXPERIMENTAL:

The analyzed manuscript forms part of the book *Lubab al-Ta'wilfi ma'ani al-tanzil*, written by *Al-Jazin* in the 14th century. It contains a women's scene represented in the *hamman* and, in the other side, comments of the *aleyas* 68 and 69 of the *azora* of the bee (*Figure 3*).
The experiments were performed directly on the manuscript. The dispersive integrated Horiba Jobin-Yvon LabRam HR800 Infinity Raman system was employed for collecting the Raman spectra. We have mainly used the laser emitted at 785 nm to minimise fluorescence of the organic medium or of the pigments/dyestuffs themselves (*Figure 1*).
XRF experiments were performed using a portable system, designed and constructed recently at the Centre de Recherche et de Restauration des Musées de France (C2RMF), which combines XRF and XRD in the same apparatus (*Figure 2*).

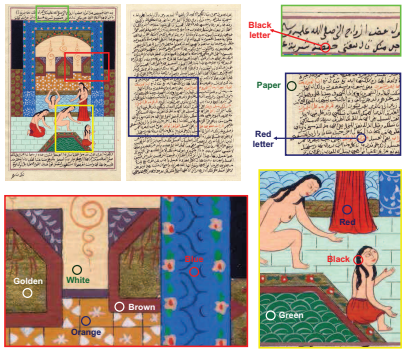

Figure 3.- Images of the studied manuscript and measurements zones

RESULTS AND DISCUSSION:

PAPER AND BACKGROUND: The XRF spectra collected on a zone of the manuscript where colour is absent showed the presence of a noticeable amount of calcium (*Figure 4*). The most likely possibility would be the presence of calcite, produced from the carbonatation of lime, which is usually employed in parchment manufacture. A common observation in all the coloured zones studied by XRF was the presence of calcium, titanium and zinc, an also barium in almost all the cases.

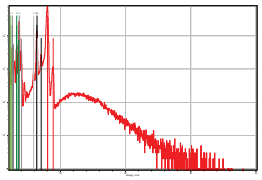

Figure 4.- XRF spectrum of the paper

WHITE COLOUR: The presence of calcium, barium, titanium and zinc was detected by XRF (*Figure 5*) in zones of white colour. Calcite was identified in these zones based on the observation of the characteristic Raman bands at 1087 cm^{-1}. Titanium dioxide (anatase) and barite were detected due to their main Raman bands at 141, 193, 392, 447, 511 and 634 cm^{-1}, and at 989 cm^{-1}, respectively (*Figure 6*). Titanium dioxide (rutile) and zinc oxide (bands at 433 and 377 cm^{-1}) were also identified in other zones of white colour, together with those mentioned before (*Figure 7*).

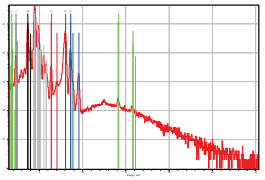

Figure 5.- XRF spectrum collected on a white colour zone

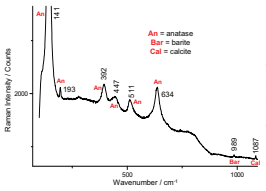

Figure 6.- Raman spectrum collected on a white colour zone

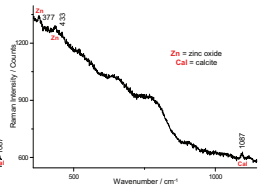

Figure 7.- Raman spectrum collected on other white colour zone

Calcite and barite must be seen as extenders and fillers of the other pigments. Zinc white (zinc oxide) and titanium white (titanium oxide) replaced lead white in artworks at the beginning of the 20th century.

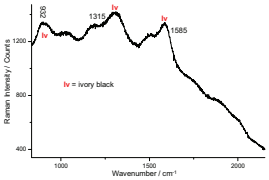

Figure 8.- Raman spectrum collected on the black letter

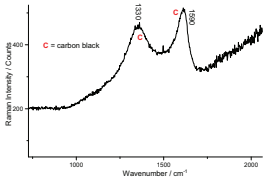

Figure 9.- Raman spectrum collected on a black area

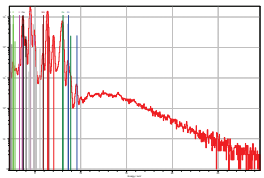

Figure 10.- XRF spectrum collected on the black zone

BLACK COLOUR: The micro-Raman study of the black letters showed curves typical of ivory black with bands at 932 ($\nu_1(a_1)$ PO_4^{3-}), 1315 and 1585 cm^{-1} (*Figure 8*). In the black areas of the illuminated manuscript, Raman spectra showed clearly the presence of carbon-based black (*Figure 9*). No characteristic chemical elements were found neither in the black letter nor in other black areas (*Figure 10*). Light elements such as phosphor or carbon are not detected due to the strong absorption in the Be window and in air (2-3 cms) between samples and XRF detector. XRF spectrum collected on the black letters did not show the presence of Ti, Zn and Ba.

RED COLOUR: Vermilion was detected by Raman micro-espectroscopy in the spectra collected on the red letter (*Figure 11*). A modern synthetic red colorant (ß-naphtol) has been detected in some red and brown zones (*Figures 12 and 13*). The experimental bands (1586, 1554, 1485, 1451, 1395, 1336, 1288, 1266, 1238, 1224, 1188, 1155, 1123, 1092, 1039, 892, 768, 737, 709, 623, 593, 513 and 313 cm^{-1}) match very well with those from the azo-pigment (ß-naphtol) standard (*Table 1*). Also, bands corresponding to anatase and rutile (bands at 609, 445 and 245 cm^{-1}), calcite, barite, vermilion (252 cm^{-1}) and red earth (iron oxide, clays and silica, bands at 281 and 402 cm^{-1}) were observed (*Figures 12 and 13*). XRF spectra performed on the red areas showed the presence of high amounts of calcium, barium, titanium, iron and also, little of mercury (*Figure 14*).

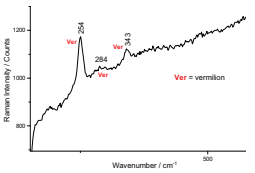

Figure 11.- Raman spectrum collected on the red letter

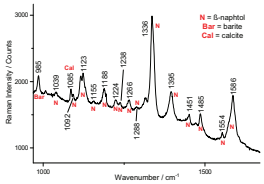

Figure 12.- Raman spectrum on a red zone

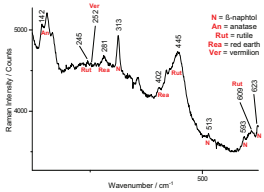

Figure 13.- Raman spectrum on a red zone

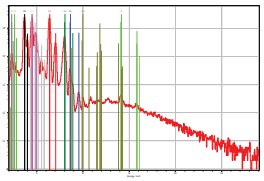

Figure 14.- XRF spectrum on a red zone

BROWN AND ORANGE COLOURS: Similar XRF spectra were collected on brown and orange zones of the manuscript; iron quantity is very high (*Figure 15*). Hematite (iron oxide) was clearly identified in the brown zones thanks to its distinctive Raman spectrum with bands at 224, 244, 293, 408, 496 and 611 cm^{-1} (*Figure 16*). Calcite, anatase and rutile were also detected. Raman spectrum collected on an orange zone showed the presence of bands at 245, 300, 388, 418, 483, 551 and 1008 cm^{-1}, attributed to yellow ochre (goethite, clays and silica), an also those corresponding to anatase, calcite, barite and the modern dyestuff detected previously in red zones: ß-naphtol (*Figure 17*).

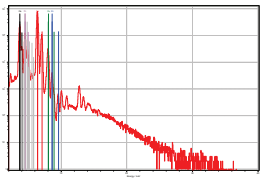

Figure 15.- XRF spectrum collected on an orange zone

Dyestuff (standard)	Raman bands (cm^{-1})
ß-naphtol (azopigment)	1587, 1554, 1487, 1451, 1396, 1338, 1288, 1266, 1239, 1224, 1189, 1156, 1124, 1093, 1041, 986, 942, 893, 838, 769, 737, 709, 654, 624, 593, 514, 466, 420, 403, 358, 340, 313, 208, 167
Chlorinated copper phtalocyanine (pigmosol green)	1528, 1436, 1380, 1332, 1274, 1205, 1140, 1075, 972, 811, 770, 737, 680, 639, 288
Copper phtalocyanine	1525, 1448, 1336, 1303, 1217, 1182, 1141, 1106, 951, 830, 776, 746, 679, 592, 484, 255, 172

Table 1.- Theoretical Raman bands of some modern organic dyestuffs

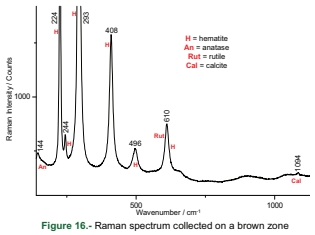

Figure 16.- Raman spectrum collected on a brown zone

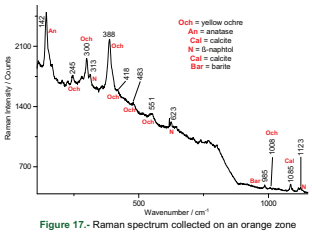

Figure 17.- Raman spectrum collected on an orange zone

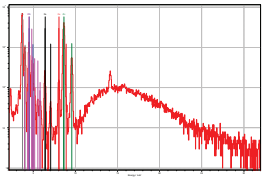

Figure 18.- XRF spectrum collected on a blue zone

GREEN AND BLUE COLOURS: Copper was detected in green and blue coloured zones by XRF (*Figure 18*). We have used a 750 µm Al filter placed at the exit of the X-ray tube, which allows to absorb all X-rays up to copper emission lines from the tube. In this form, Cu K photons collected come only from the sample. Raman spectrum collected on a green area showed strong characteristic bands at 1530, 1439, 1332, 1277, 1207, 772, 739 and 682 cm^{-1} (*Figure 19*), that match the Raman spectra features of chlorinated copper phtalocyanine (pigmosol green) (*Table 1*). Similarly, copper phtalocyanine (bands at 1527, 1450, 1339, 1306, 1142, 1107, 952, 830, 778, 746 and 679 cm^{-1}) was detected in blue areas (*Figure 20 and Table 1*). In these zones, rutile, calcite, anatase and barite were also detected.

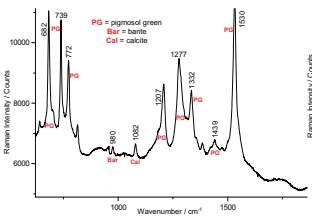

Figure 19.- Raman spectrum collected on a green zone

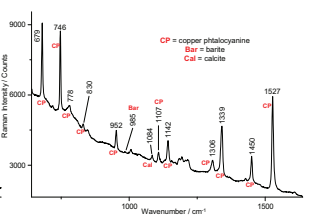

Figure 20.- Raman spectrum collected on a blue zone

CONCLUSIONS:

The palette used to illuminate the manuscript and to write the text were completely characterized. The materials identified in the text (letters) were the following: vermilion, ivory black and possibly calcite. For the image, we have observed the presence of anatase, rutile, calcite, barite, zinc oxide, carbon black, red earth, hematite, yellow ochre, β-naphtol and copper phtalocyanine and derived compounds. The detection of titanium oxides (anatase and rutile), barium sulphate (barite) and organic synthetic colorants such as β-naphtol or copper phtalocyanine (and chlorinated copper phtalocyanine) only in the image provide an indisputable indication for either forging (later than 14th century) or for the possibility of repainting or retouching after 19th century in some zones of the manuscript. However, it is possible that the written text could be original (from the 14th century).