"ILLUMINATED MANUSCRIPTS CHARACTERIZATION BY LABORATORY-MADE PORTABLE XRD AND MICRO-XRD SYSTEMS"

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INTRODUCTION AND AIM OF THE WORK:

The study of illuminated manuscripts has become one of the most important subjects within cultural heritage due to their historical and artistic importance. In this sense, the heritage left by the Arab world in the history of sciences and arts is directly related to the documentary sources, including manuscripts. Nowadays, non-destructive techniques such as μ-Raman and X-rays fluorescence are generally performed most for the analyses of this type of artworks, while μ-FTIR spectroscopy and Mössbauer spectroscopy were also proved to be useful. Until now, the new portable X-ray diffraction / X-ray fluorescence and micro-diffraction laboratory equipments have been tested for paintings, ceramics, metals, etc, but they have never been used to study illuminated manuscripts, where the quantity of material is minor. Our special focus in this work will be to report on novel results from two Arabic manuscripts from XIVth century and to prove the validity of the new X-ray diffraction systems for the study of manuscripts.

Experimental set-up of the XRD/XRF portable system employed by manuscripts analyses

Experimental set-up of the μ-XRD system employed by manuscripts analyses

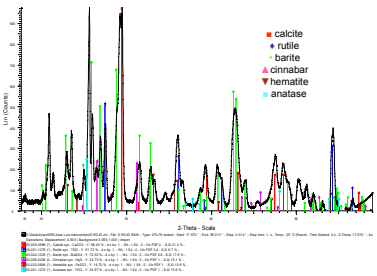
EXPERIMENTAL:

The two analyzed manuscripts are part of the book *Lubab al-Ta'wilfi ma'ani al-tanzil*, written by Al-Jazin in the XIVth century. The rectum of one of the pages detached from the manuscript contains the commentary of the *aleyas* 68 and 69 of the *azora* of the bee; in the verse, a women's scene is represented in the *hamman*.

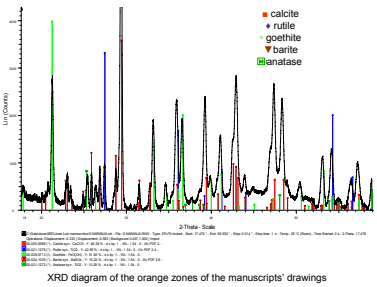
The experiments were performed directly on the manuscript, in reflection mode by the portable XRD/XRF system and in transmission mode by μ-XRD. In both cases, X-rays tube with copper anode were used for and the data were collected with imaging plates as 2D detectors. In the portable system, the experiments were performed using XRD and XRF simultaneously. The measured areas were about 3 mm^2 for the portable system and 0.2 mm^2 for micro-diffraction using a collimator of 200 μm. Also, some μ-Raman measurements were performed using green (531.9 nm) and red (632.8 nm) lasers; in this case, the size of the analysed zone is approximately 25 $μm^2$.

RESULTS:

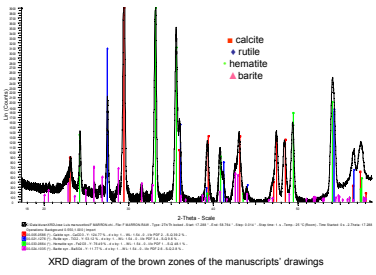
PAPER AND PREPARATION LAYER: A common observation in all the cases was the presence of calcite by XRD. XRF spectrum from the paper showed the presence of high amount of calcium. Also, titanium oxide (rutile) by XRD and high contents of zinc by XRF were found in all the zones analysed.



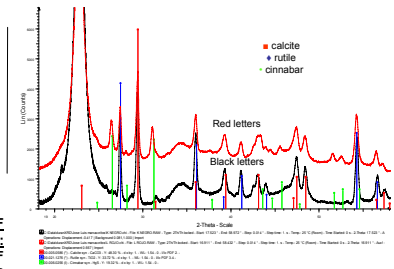
XRD diagram of the red zones of the manuscripts' drawings



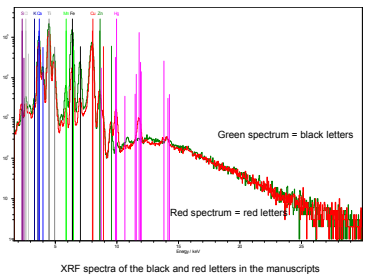
XRD diagram of the orange zones of the manuscripts' drawings



XRD diagram of the brown zones of the manuscripts' drawings



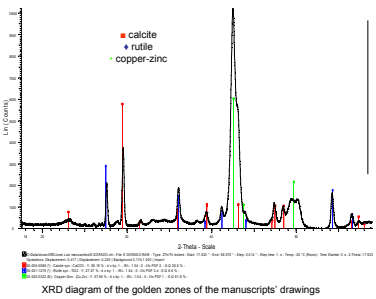
XRD diagrams of the black and red letters in the manuscripts



XRF spectra of the black and red letters in the manuscripts

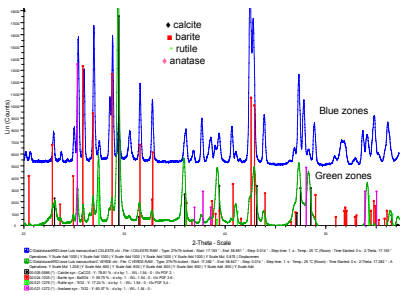
LETTERS: The presence of mercury and sulphur by XRF were detected in the red letters, and cinnabar by XRD. Characteristic chemical elements of pigments by XRF and compounds responsible for the black colour by XRD were not found in the black letters. Curves typical of ivory black were collected by μ-Raman. Light elements such as carbon or phosphor are not detected by XRF due to the strong absorption in air between specimen and detector.

GOLDEN AREAS OF THE DRAWINGS: Experiments by XRF showed the presence of zinc and copper. Analysis by XRD showed the presence of brass (Cu-Zn alloy).

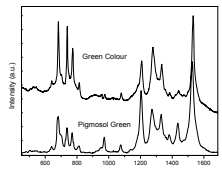


XRD diagram of the golden zones of the manuscripts' drawings

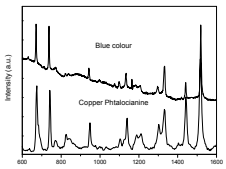
GREEN AND BLUE COLOURS OF THE DRAWINGS: Diffraction patterns attributed to crystalline inroganic pigments were not found in blue and green colours; phases of calcite and rutile, as usual, and in addition, those corresponding to barite and anatase, were detected in both colours. By Raman, we detected the presence of two modern organic pigments: pigmasol green (chlorinated copper phtalocyanine) and copper phtalocyanine)



XRD diagrams of the green and blue zones of the manuscripts' drawings



Raman spectra of the green zones in the manuscripts and comparison with standard

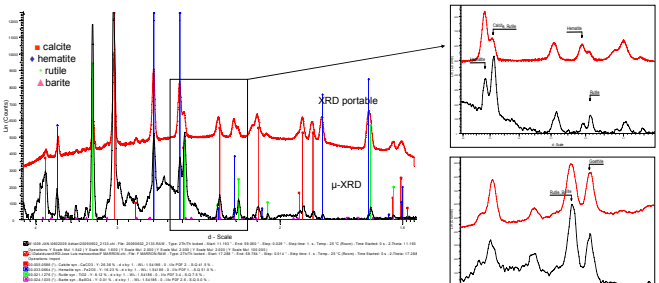


Raman spectra of the blue zones in the manuscripts and comparison with standard

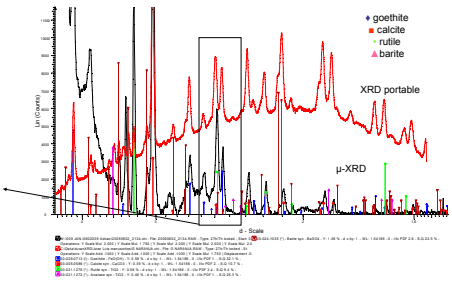
DISCUSSION:

The phases identified by μ-XRD are the same that those found with the XRD portable system. The minor values for the beam divergence in the μ-XRD Rigaku apparatus (3.2 mrad) in comparison with the divergence of the policapillary semi-lens of the portable XRD equipment is the responsible for the better resolution in the diagrams collected by the first system. Increases of the relative intensities in the patterns of the compounds coming from the paper (calcite) and preparation layer (rutile) were observed by μ-XRD. In the case of the experiments performed by the portable XRD system, higher relative intensities were detected in the patterns of the pigments (hematite, goethite, cinnabar or brass).

RED, ORANGE AND BROWN COLOURS OF THE DRAWINGS: A high content in iron was detected by XRF in all these zones, also mercury was present in the red colour. XRD diagram showed the presence of cinnabar and hematite in the red zones, in addition, barite and anatase were detected. Goethite and hematite phases were clearly detected by XRD in the orange and brown colours, respectively; barite in both colours and anatase in the first one were also found.



XRD diagrams of the brown zones of the manuscripts' drawings performed by μ-XRD and XRD portable sytems



XRD diagrams of the orange zones of the manuscripts' drawings performed by μ-XRD and XRD portable sytems

CONCLUSIONS:

This work shows the validity of the laboratory made non-destructive portable XRD and μ-XRD systems for the study of illuminated manuscripts, although the amount of colouring material is very small.

We have detected the presence of calcite, titanium oxide (rutile and anatase) and barite, possibly used in the manufacture of the paper and in the preparation layer for the manuscripts; and also, hematite, goethite, cinnabar, brass and phtalocyanine as colouring materials. The presence of titanium oxide, barite and phtalocyanine compounds demonstrate that the drawing of the manuscript was retouched after 19th century. Differences betwen the results obtained by both techniques due to acquisition mode are shown.

X-Ray attenuation length (μm)	γ = 90° (transmission)	γ = 10° (reflection)
Fe_2O_3 (hematite)	9.90	1.72
HgS (cinnabar)	7.20	1.24
FeOOH (goethite)	13.70	2.40

X-rays attenuation lenght (depth into the material where the intensity of X-rays falls to 1/e of its value at the surface) in the pigments found in the manuscripts at E=8.4 keV (Cu Kα)

The values of X-rays attenuation lenght in some of the pigments found in the manuscripts, obtained using an incidence angle of 90º in transmission mode by μ-XRD, are around six times higher than those gained with an incidence angle of 10º by the portable XRD system. In the case of transmission experiments, X-rays have penetrated into the core of the manuscript. The penetration is minor in the experiments performed in reflection mode, in this case, the more superficial compounds (pigments) have been the most manifestly observed.