

LIBS AND XRF INVESTIGATION OF PAINTINGS' MATERIALS: A PRELIMINARY STUDY

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Introduction

Paintings are characterized by their multilayered structure. For instance, wooden panels are usually covered by gesso (ground) on which multiple paint layers are applied in the framework of medieval panel painting techniques (Thompson 1998). Similar techniques are more or less employed in the framework of Greek religious icons' construction (Kontoglou 1993). However, this particular structure can impose difficulties in the analytical investigation of pertinent artifacts, especially when techniques with depth-dependent output are employed. In the current study authors explore the potentialities of the hitherto underused in the field of paintings' investigation Laser Induced Breakdown Spectroscopy (LIBS) in comparison with the well-established X-ray fluorescence spectroscopy (XRF) (Botto et al. 2019, Burgio et al. 2001, Mantler & Schreiner 2000). In this framework, a series of mock-up samples were manufactured following traditional post-byzantine painting techniques (Figure 1). These samples were subjected to analysis by XRF and LIBS, and the corresponding experimental results were evaluated in view of resolving possible depth-dependence of the LIBS and XRF signals (Figures 2, 3). It is shown that through the proper manipulation of experimental conditions and data, one can extract information pertaining to the depth profile of relevant paintings.

The mock-up samples

Mock-up samples were made by following the typical post-byzantine painting techniques i.e. on a wooden panel covered with gesso (i.e. gypsum+gelatin) paint layers (pigment+egg yolk) were applied. The selected pigments were orpiment (As_2S_3) cinnabar (HgS) and white lead ($2PbCO_3 \cdot Pb(OH)_2$) that were rather frequently employed by Greek post-byzantine painters.

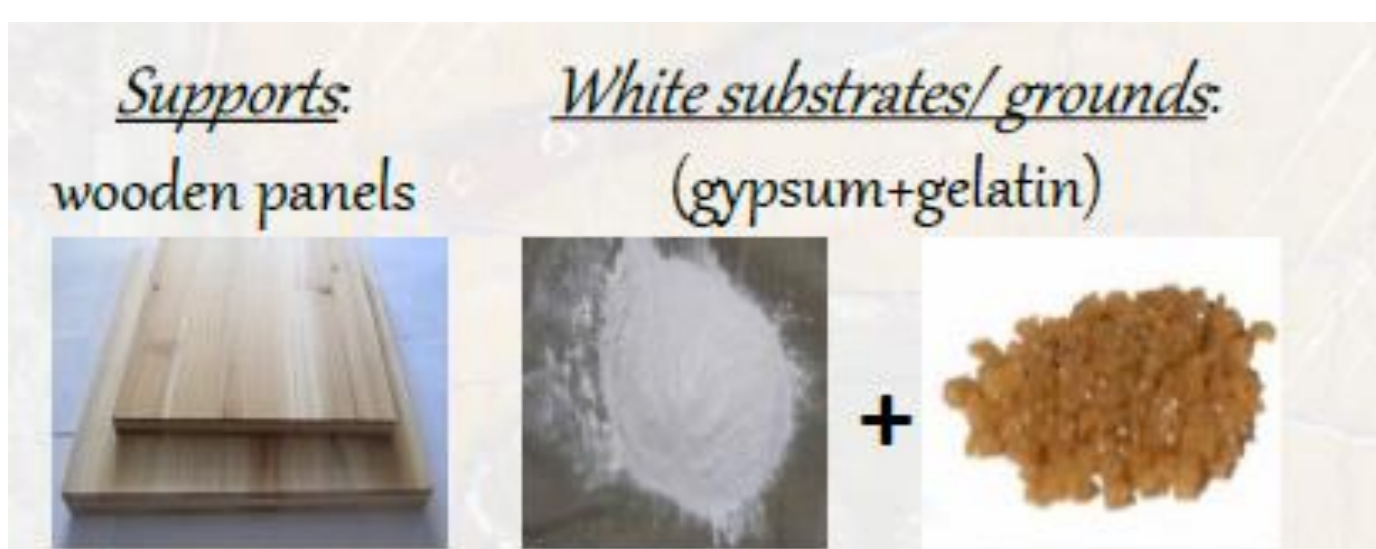


Fig. 1a. Left) Bare wooden panel; middle and right) gesso raw materials.



Fig. 1b. Left to right: the process of mixing pigments with egg yolk and painting.



Fig. 1c. Left) Orpiment and cinnabar, grinded pigments. Right) The mock-up panel painting and the corresponding index of the various multilayered samples.

As	Hg	Pb
Hg	As	Pb
Pb	As	Hg
As	Hg	Pb
Hg	Pb	As
Pb	Hg	As
As	Pb	Hg
Hg + As	Pb + As	Pb + Hg
Pb	Hg	As
As	Hg	Pb
Pb + Hg	Pb + As	Hg + As

X-ray Fluorescence spectroscopy (XRF)



Fig. 2a. MA-XRF scanner. M6 Jetstream (Bruker)

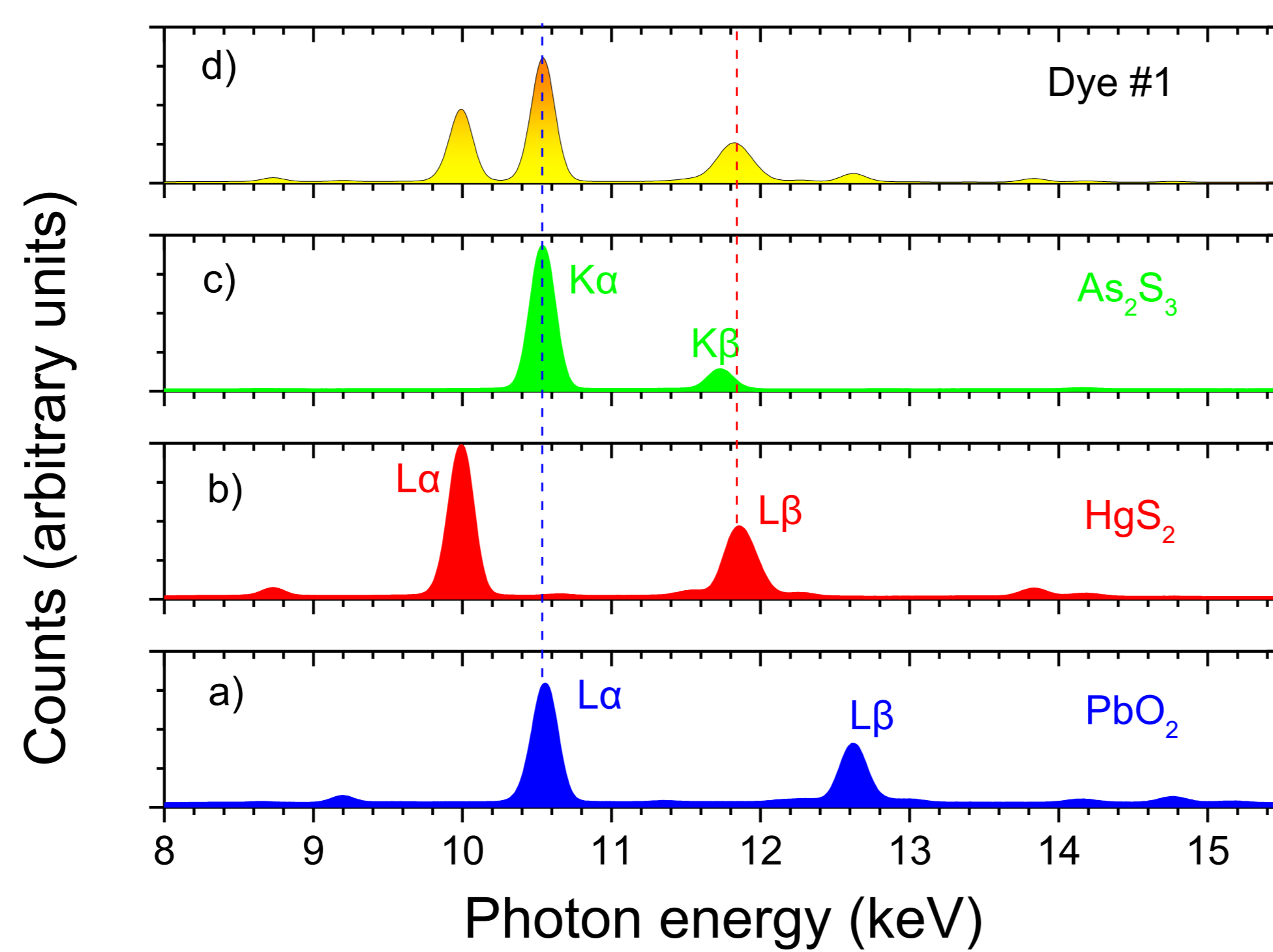


Fig. 2b. XRF spectra from: a) pure lead white, b) vermilion, c) orpiment and d) from the dye #1 square (upper left corner of the mock-up panel, Fig. 1c).

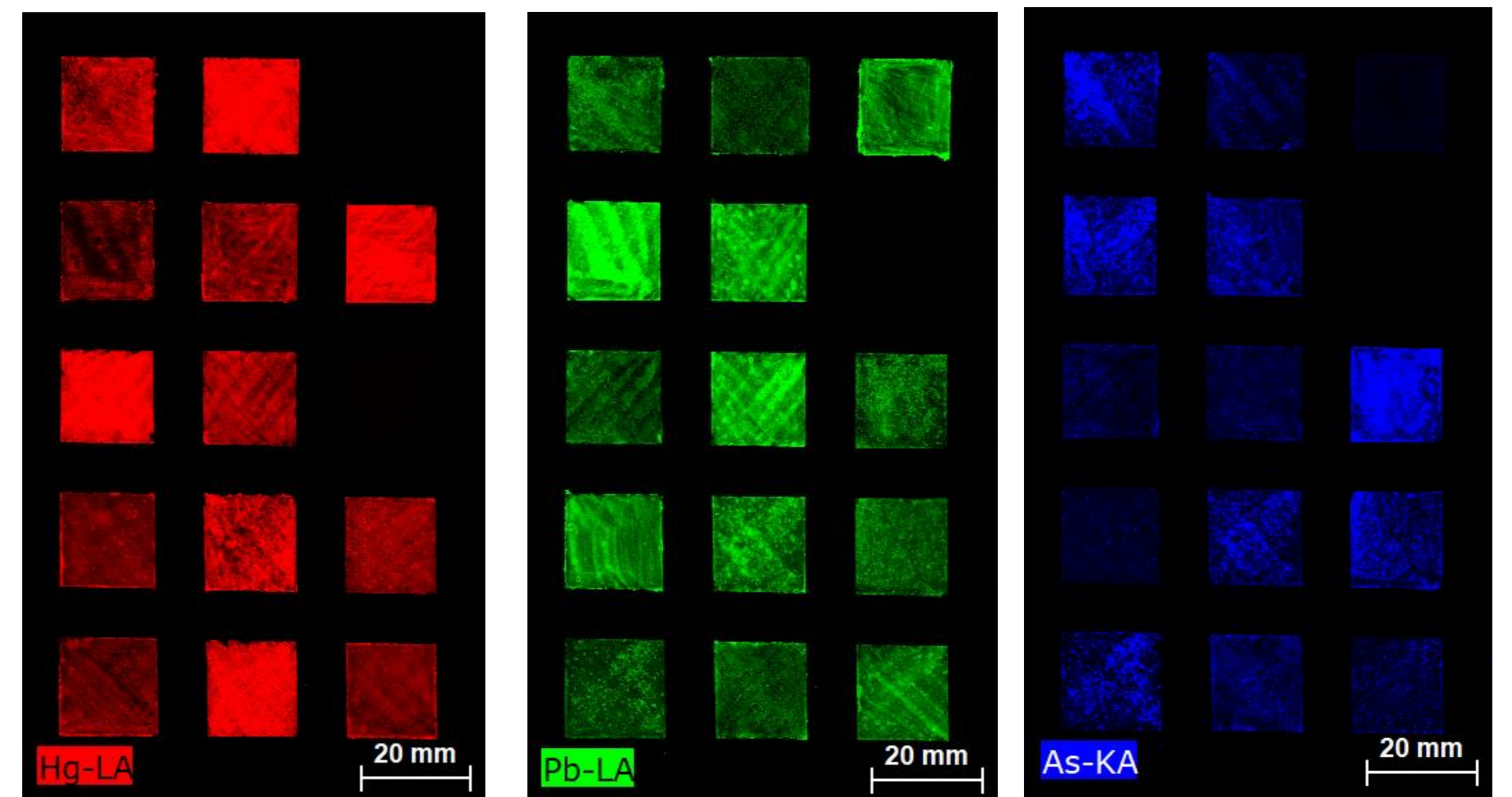


Fig. 2c. The application of the macroscopic XRF allowed the extraction of the elemental distribution maps of the elements characterizing the three pigments: mercury for cinnabar (left), lead for lead white (center) and arsenic for orpiment (right). The extracted elemental maps coincide with the spatial distribution of the mock-up samples, despite the energy proximity of the X-ray characteristic transitions. Nevertheless, the overlap of the transition lines prohibits any prediction concerning the in-depth distribution of the pigments.

Laser Induced Breakdown Spectroscopy (LIBS)

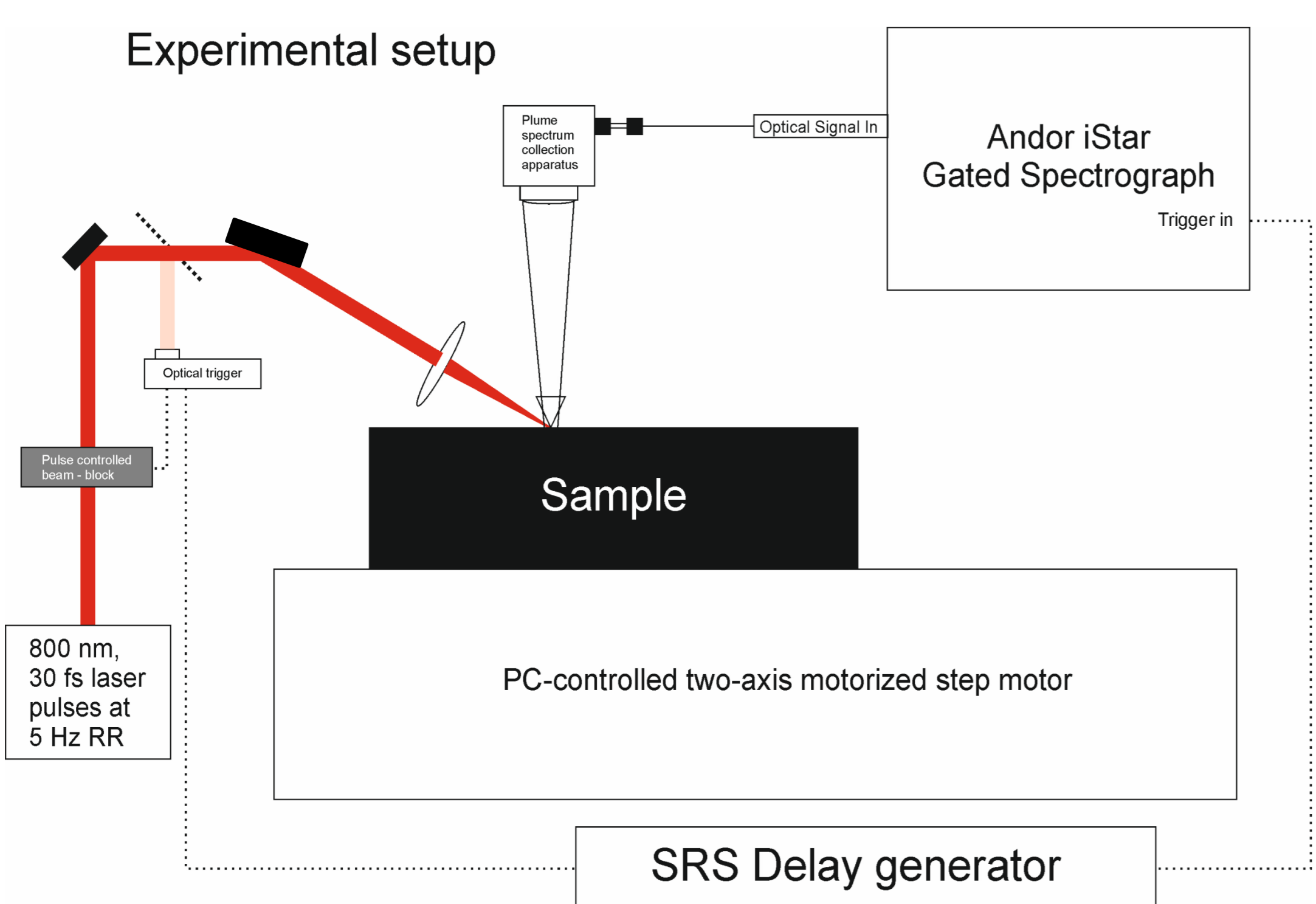
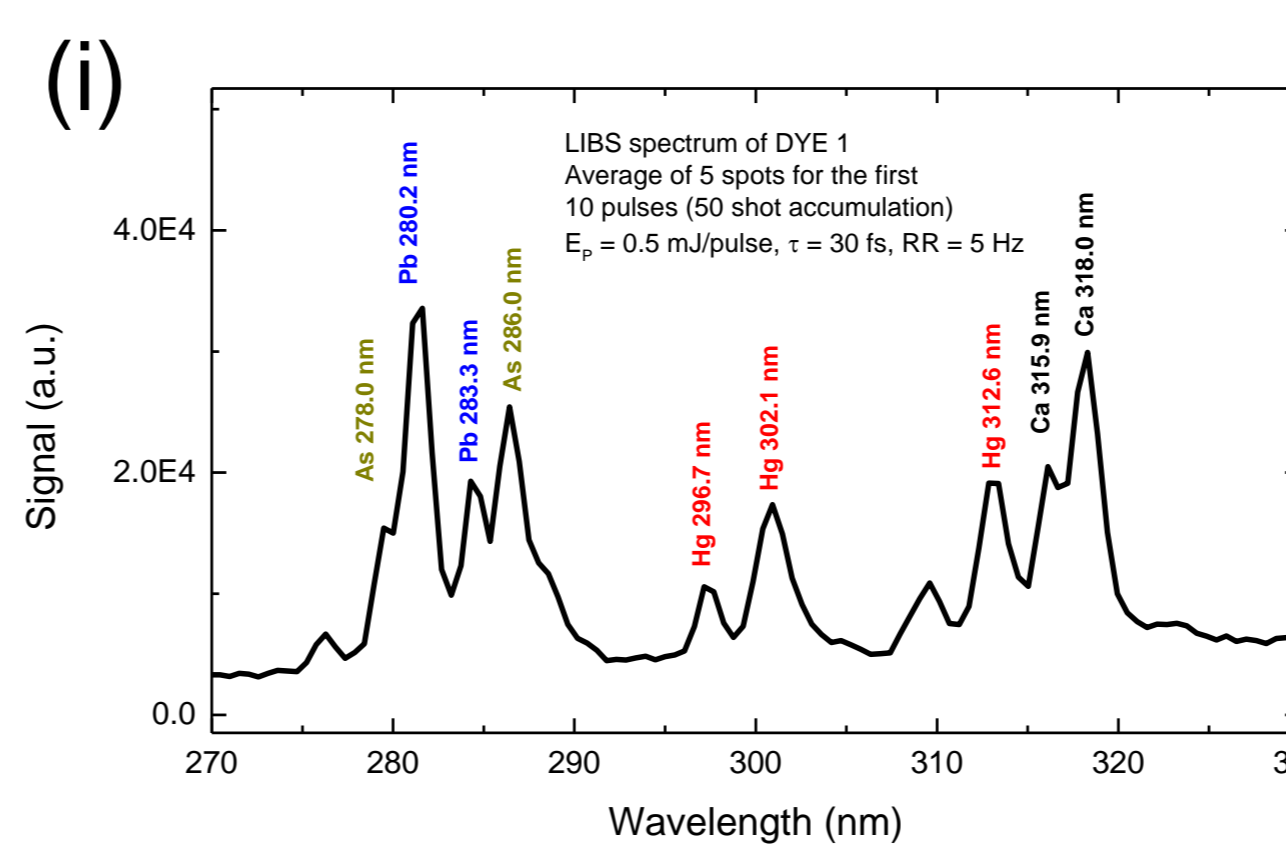


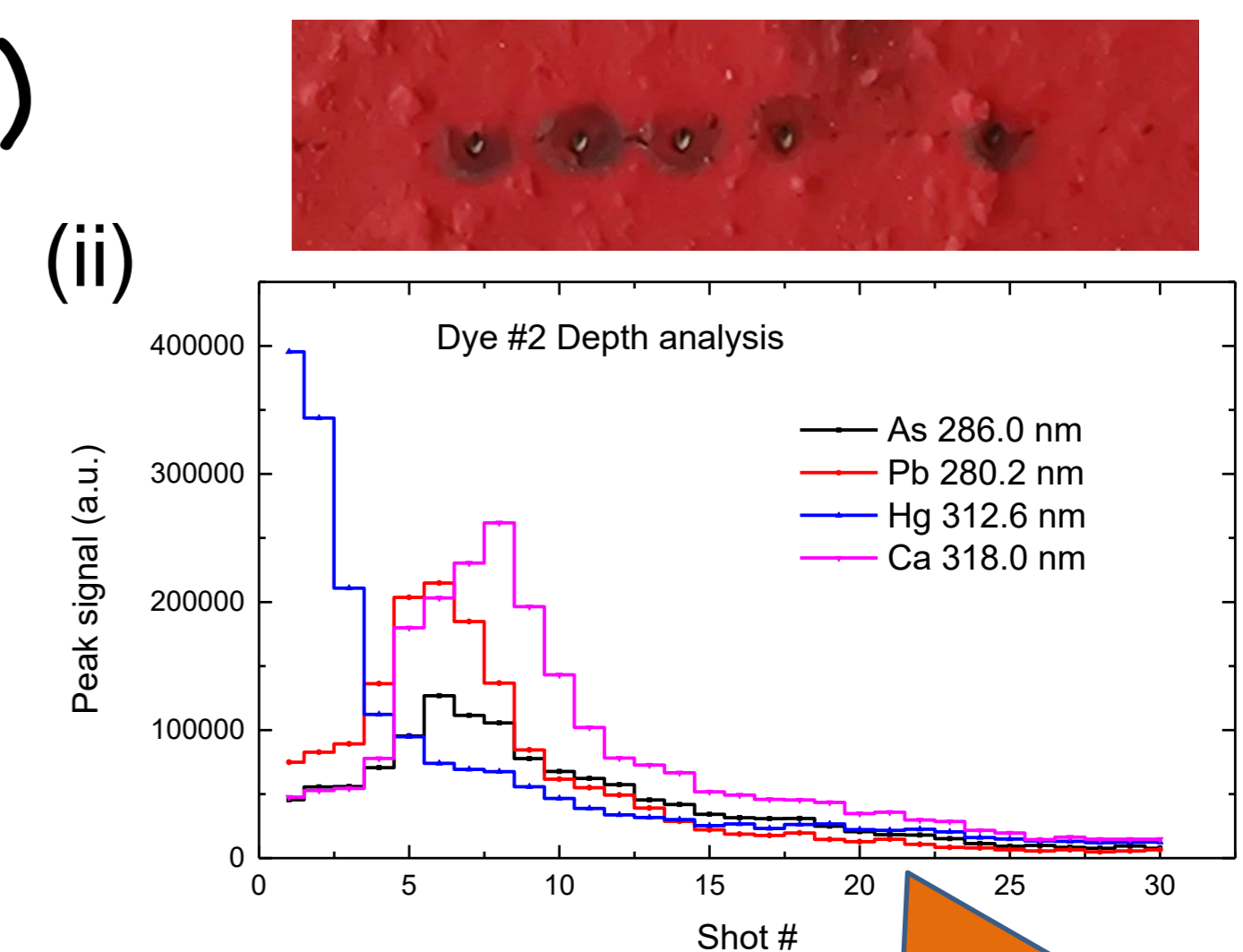
Figure 3a: Experimental setup. A pulsed laser is focused by a lens ($f = 15$ cm) onto the surface of the sample. A delayed pulse triggers the gated spectrograph. The delay is estimated as $1/RR + 4$ ns and the total acquisition time is equal to 10 ns. By doing so, no ambient light or radiation originating from the laser beam is detected.



Part of the plume's emission spectrum, where atomic lines of Mercury (Hg), Calcium (Ca), Lead (Pb) and Arsenic (As) are present. Such data could be useful to distinguish between lead and arsenic, since XRF methods present difficulties to do so.

Figure 3b:

(i) Typical spectrum of the plume that results from the ablation of the dye. The presented spectrum results from the average of 5 regions of the dye (10 laser pulses per region) for a total of 50-shot average.
(ii) Signal of each atomic line as a function of laser shot number. It is evident that in the first few spectra, mercury's atomic lines appear stronger, while for later shots (lower paint layers), lead and arsenic atomic lines are dominant.



The layering of pigments in DYE #2 is seen when the signal of the emission lines of the elements is plotted as a function of the laser shot number. A clear presence of Mercury in the top layer of the dye is observed, while Arsenic and Lead are found at lower depths. The base (white) layer, contains Calcium which is found in lower layers than the other elements. The almost simultaneous presence of lead and arsenic is due to granulation of the orpiment pigment (As_2S_3).

Conclusions

The potentialities of the LIBS and MA-XRF techniques for pigment characterization are explored. Mock-up samples were manufactured containing the pigments orpiment, cinnabar, and lead white, in any possible combination of mix and layer. The MA-XRF allowed the extraction of the elemental distribution maps of the elements characterizing the three pigments. Nevertheless, the overlap of the transition lines prohibits any prediction concerning the in-depth distribution of the pigments. Similarly, the application of LIBS allows composition determination for each mock-up sample. But moreover, LIBS allowed the in-depth study of the pigment distribution in exchange for the micro destruction of the examined area. Analysis of the optimal LIBS experimental conditions to improve the in-depth spatial resolution and to diminish the laser spot size is on the way.

References

- Botto A., Campanella B., Legnaioli S., Lezzerini M., Lorenzetti G., Pagnotta S., Poggiali F., Palleschi V., (2019), *Applications of laser-induced breakdown spectroscopy in cultural heritage and archaeology: A critical review*, Journal of Analytical Atomic Spectrometry, 34(1), 81-103.
- Burgio L., Melessanaki K., Douglteridis M., Clark R.J.H., Anglos D., (2001), *Pigment identification in paintings employing laser induced breakdown spectroscopy and Raman microscopy*, Spectrochimica Acta - Part B Atomic Spectroscopy, 56(6), 905-913.
- Kontoglou P. (1993), *Elphrasis tēs orthodoxou eikonographias* (in Greek), Astir, Athens.
- Mantler M., Schreiner M., (2000), *X-ray Fluorescence Spectrometry in Art and Archaeology*, X-Ray Spectrometry, 29(1), 3-17.
- Thompson D. V. (1956), *The materials and techniques of medieval painting*, Dover, New York.
- M. Alfeld, J.V. Pedrosa, M. van Ekema-Hommes, G. Van der Snickt, G. Tanber, J. Blaas, M. Haschke, K. Erler, J. Dik, K. Janssens, A mobile instrument for in situ scanning macro-XRF investigation of historical paintings, J. Anal. At. Spectrom. 28 (2013) 760.

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