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SUPPLEMENTARY INFORMATION: ADDITIONAL FIGURES AND TABLES

XRFast and New Software Package for Processing of MA-XRF Datasets using Machine Leaning

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Abstract

X-ray fluorescence (XRF) is a common technique in the field of heritage science. However, data processing and data interpretation remain a challenge as they are time consuming and often require *a priori* knowledge of the composition of the materials present in the analyzed objects. For this reason, we developed an open-source, unsupervised dictionary learning algorithm reducing the complexity of large datasets containing 10s of thousands of spectra and identifying patterns. The algorithm runs in Julia, a fairly new programming language, allowing for much faster data processing compared to other languages like Python and R. This approach quickly reduces the number of variables and creates correlated elemental maps, characteristic for pigments containing various elements or for pigments mixtures. This alternative approach creates an overcomplete dictionary which is learned from the input data itself, therefore reducing the *a priori* user knowledge. The feasibility of this method was first confirmed by applying it to a mock-up board containing various known pigment mixtures. The algorithm was then applied to a macro XRF (MA-XRF) data set obtained on an 18th century Mexican painting, and positively identified smalt (pigment characterized by the co-occurrence of cobalt, arsenic, bismuth, nickel, and potassium), mixtures

of vermilion and lead white, two complex conservation materials/interventions. Moreover, the algorithm identified correlated elements that were not identified using the traditional elemental maps approach without image processing. This approach proved very useful as it yielded the same conclusions as the traditional elemental maps approach followed by elemental maps comparison but with a much faster data processing time. Furthermore, no image processing or user manipulation was required to understand elemental correlation. This is open-source, open-access, and thus freely available code running in a platform allowing faster processing and larger data sets represents a useful resource to understand better the pigments and mixtures used in historical paintings and their possible various conservation campaigns.

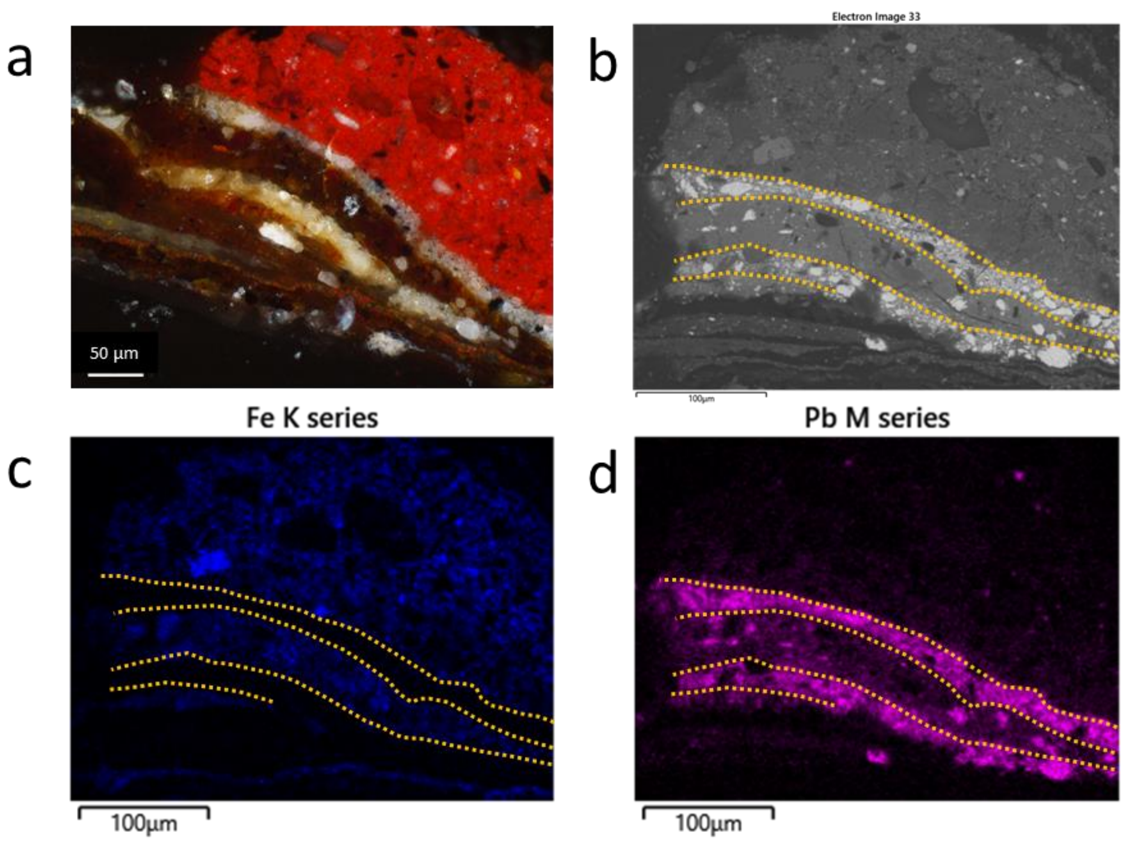

Figure S1. (a) optical microscopy image, (b) backscattered electron image of cross section taken on the edge of the painting with (c) and (d) elemental maps for Fe and Pb, showing the red Fe-rich and white Pb-rich imprimaturs below the complex stratigraphy.

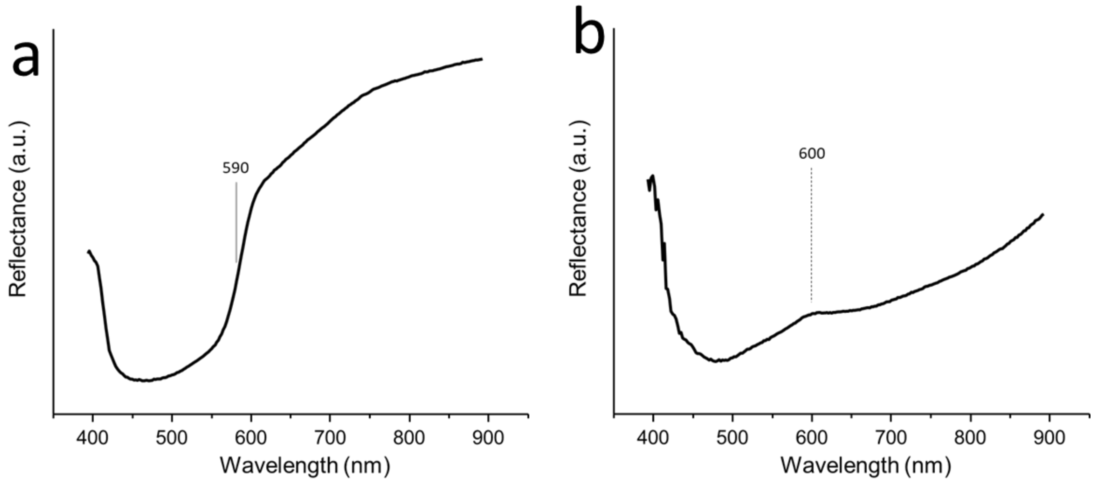

Figure S2. (a) extracted reflectance curve presenting the 590 nm characteristic inflection point for vermilion, and (b) extracted reflectance curve presenting a maximum reflectance around 600 nm and possibly associated with a Cu-containing green pigment such as verdigris or copper resinate

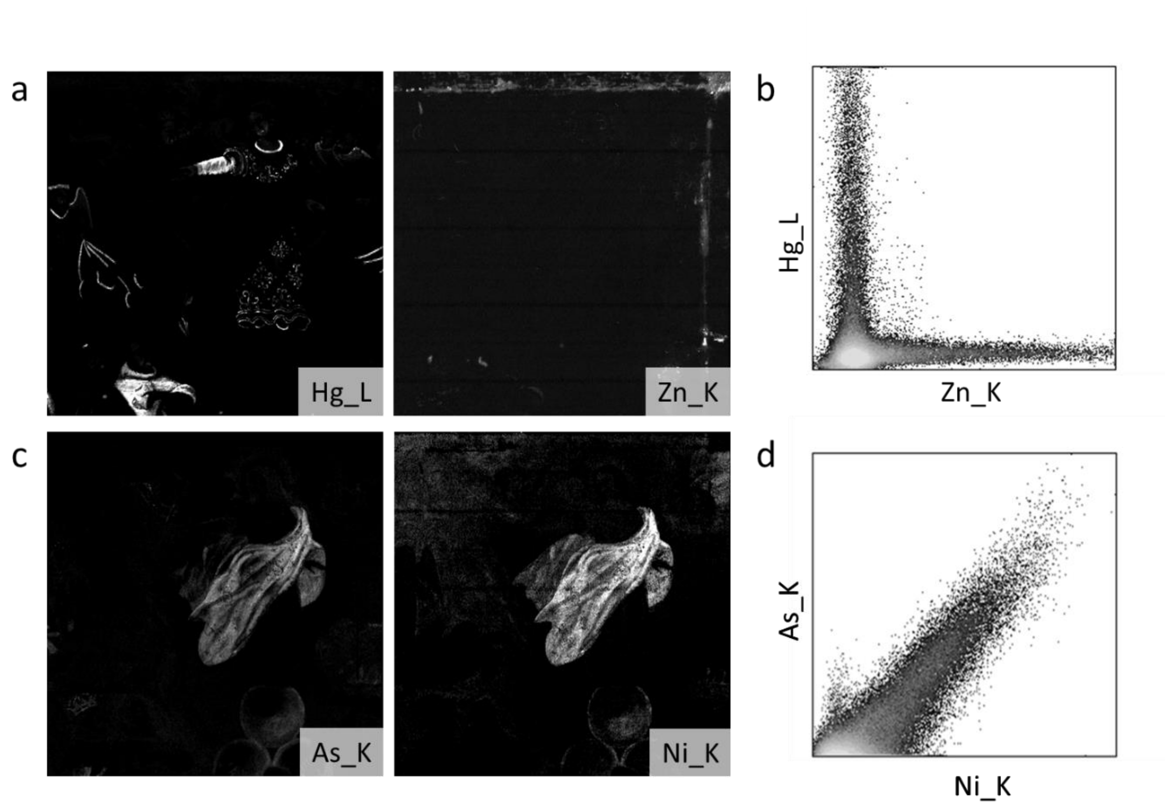

Figure S3. (a) elemental maps for Hg and Zn and (b) associated correlation plot, showing the usual pattern for non-correlated elements. (c) elemental maps for As and Ni, constitutive of smalt and (d) associated correlation plot showing the usual pattern for fully correlated elements.