Palette to Palette - an integrated study of spectroscopic analysis and UMAP on Wu Guanzhong's paint palette and his painting

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Introduction

The common 20th century modern artist palette comprises an array of synthetic inorganic and organic pigments (SOP), which are typically present only in small quantities due to their high tinting strengths, further for the SOPs minor variation in their skeletal carbocyclic ring structures, such as the presence of functional groups can significantly alter the resulting pigment hue, adds to the difficulty in their identification, usually requiring multiple complementary spectroscopic techniques. In this study, a combination of Raman microscopy, macro X-ray fluorescence (MA-XRF) and hyperspectral imaging (HSI) was performed on the paint palette of the modern Chinese artist Wu Guanzhong (1919-2010), where sampling was considered less invasive to the visual integrity of the object, and the results then build towards a paint reference library of the artist to support further studies of the artist's paintings via non-invasive data acquisition and machine learning model.

Methods

For the paint palette (Fig.1), MA-XRF data was collected with Bruker M6 Jetstream (Rh anode, 50 kV, 600 μA, air-path) then the elemental maps were generated with PyMCA (Fig.2), whilst micro-samples were collected from 13 distinctive regions of the palette that represented a different paint colour, Raman spectra (Fig.3) were collected with Reinshaw inVia™ Qontor® coupled with Lecia Microscope (50x objective, 785nm laser excitation, 10 seconds, 5 accumulations, 200-2000 cm^{-1}). For both the palette and Wu's painting *Xidi Village* (Fig.4), visible near infrared data was acquired with HySpex VNIR-1800 (400-1000 nm), then datasets from regions of interest (ROI) from each subject, the datasets were reduced by random selection at a percentage, (30% for the palette and 40% for the painting) then processed within one unsupervised learning model - Uniform Manifold Approximation and Projection (UMAP), followed by non-linear least square fitting (Fig.5).

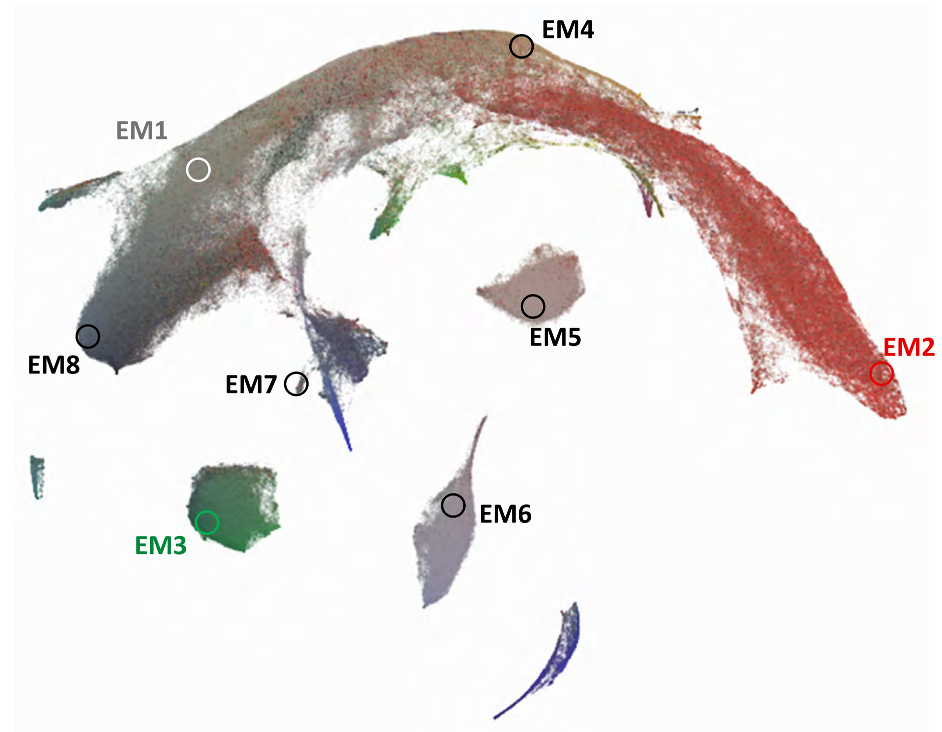

Fig.5 – UMAP scatter plot of the artist's paint palette and his painting *Xidi Village*. Each endmember (EM) represents a reflectance spectrum corresponding to a different hue of paint colour.

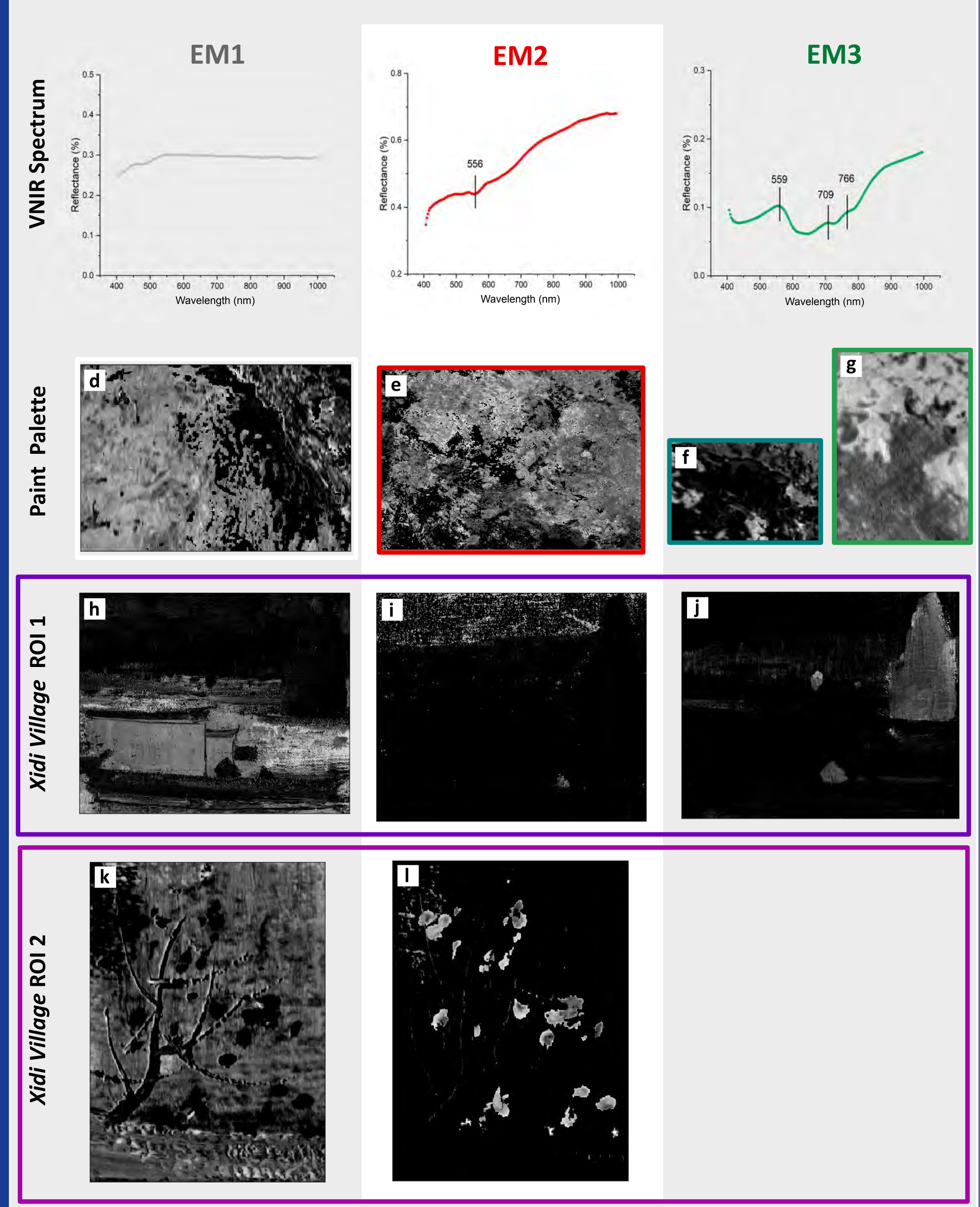

Fig.6 – The VNIR spectrum of (a-c) EM1-3 corresponds to white, red and green areas respectively and their mapped results in the corresponding areas of the palette are highlighted in (d-g) and of the painting (h-l). From the pigment results determined from the palette, these are assigned as titanium / zinc white, madder / alizarin and phthalo green.

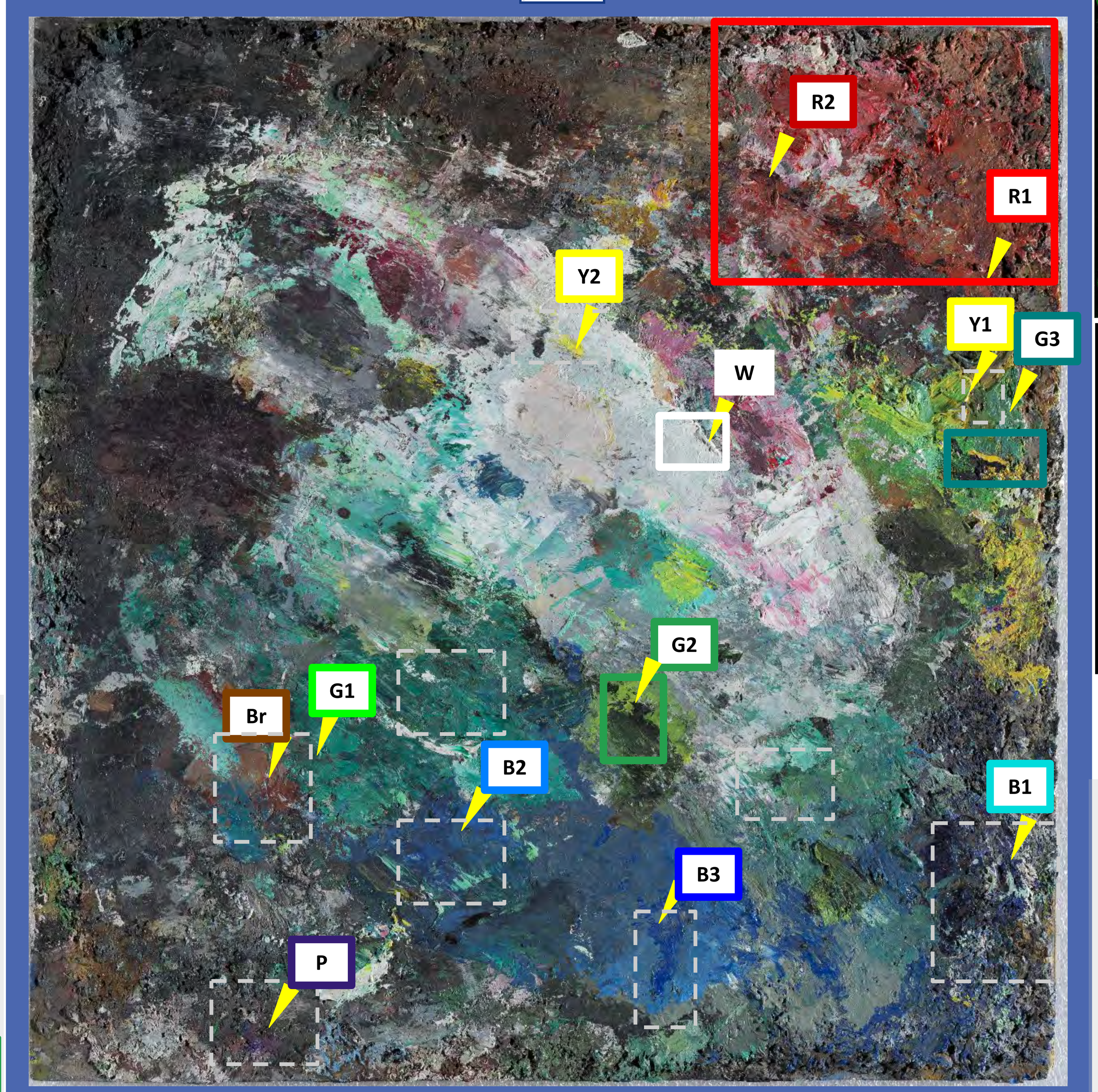

Fig.1 - Paint palette of the artist Wu Guanzhong (1990s) [FA2018.0377.001, 46 x 46 cm]†. Selected ROIs for UMAP are indicated by boxes and sampling points for Raman spectroscopy are labeled and indicated by yellow triangles. Boxes in solid lines are further discussed in Fig.6.

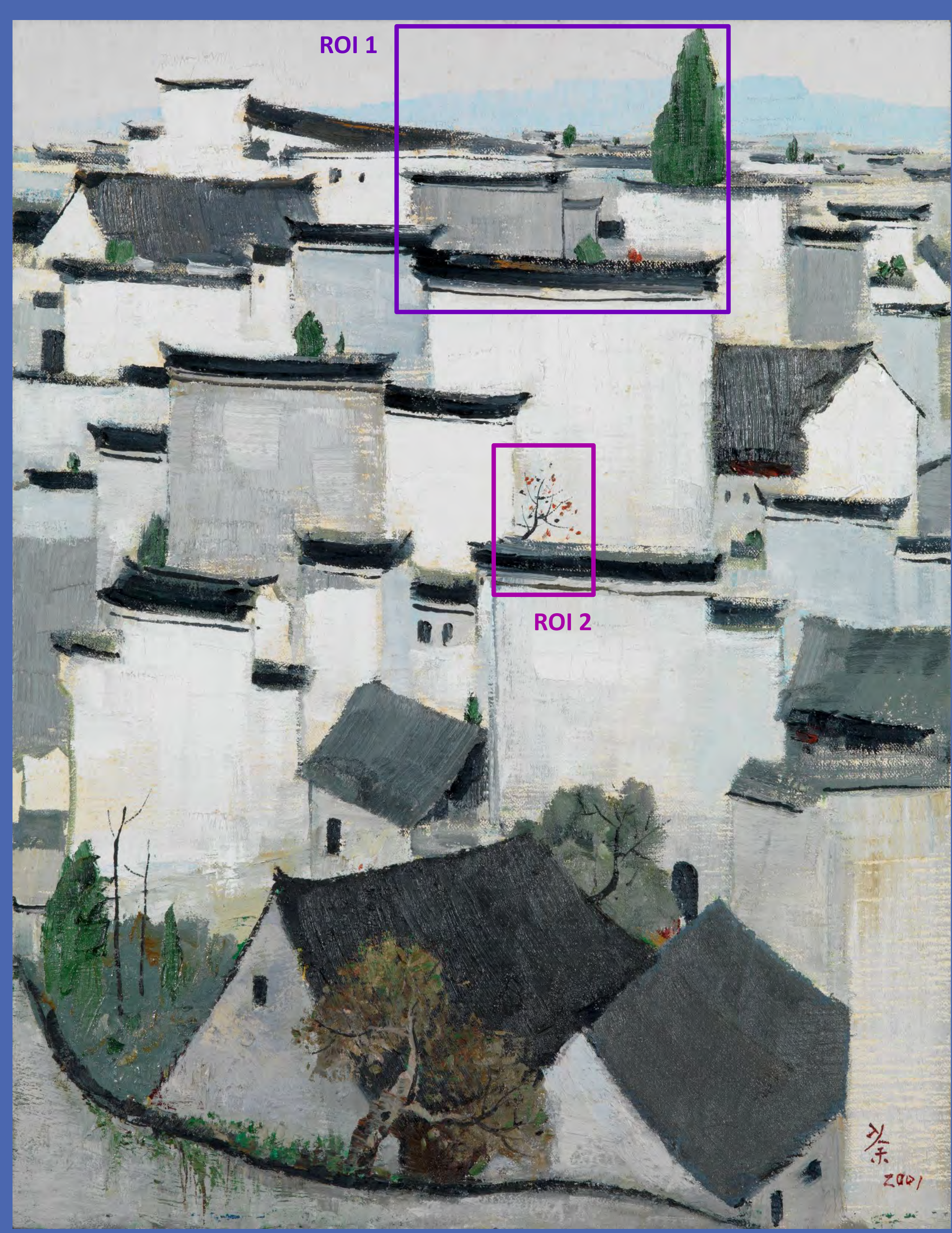

Fig.4- *Xidi Village* (2001), oil on canvas [FA2014.0016, 79.9 x 64.6 cm]†, selected ROIs for UMAP are indicated by boxes and labelled.

† From the Wu Guanzhong collection of the Hong Kong Museum of Art (HKMoA)

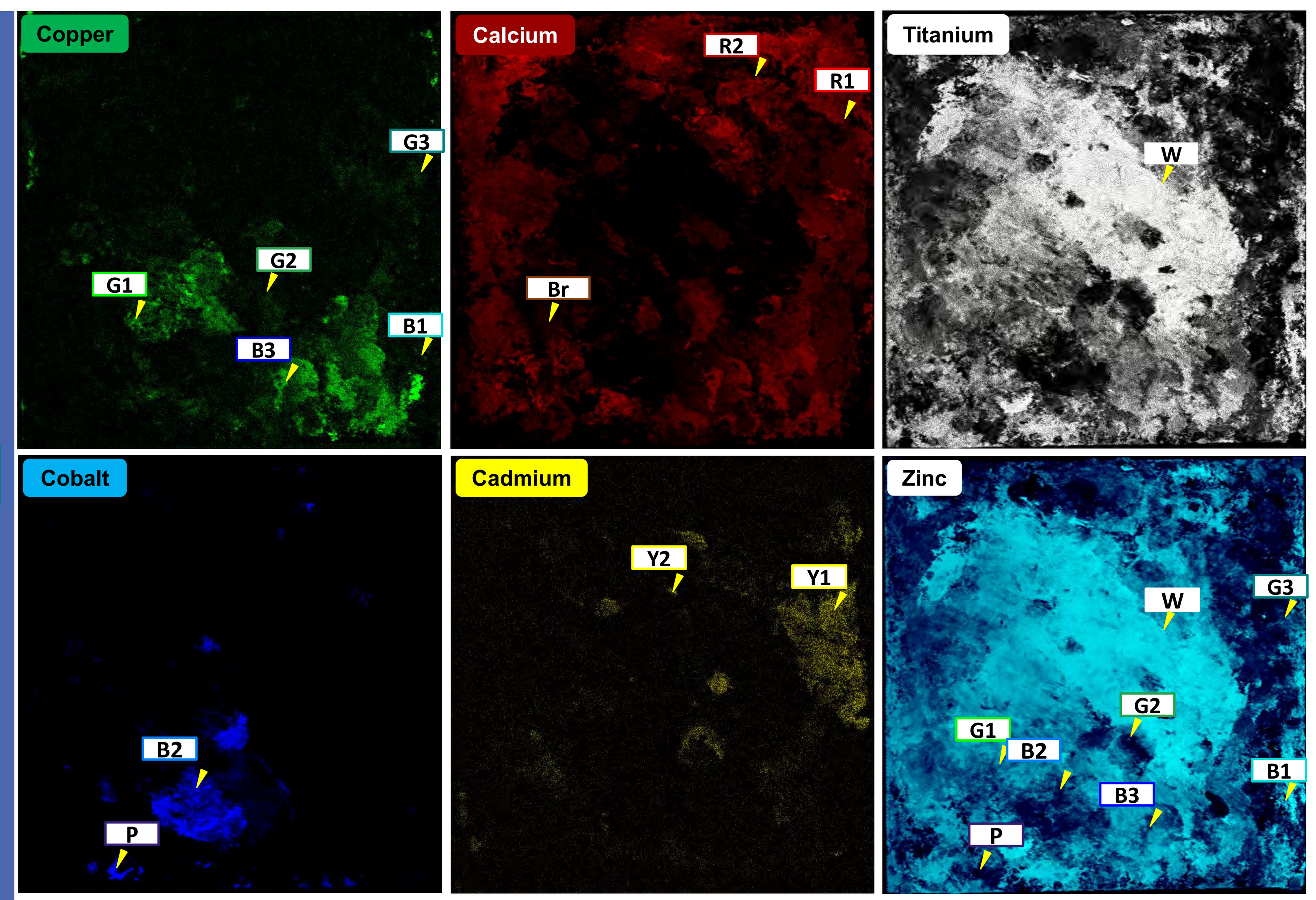

Fig.2 - Selected XRF elemental maps of the paint palette with sampling points for Raman spectroscopy which are indicated by yellow triangles.

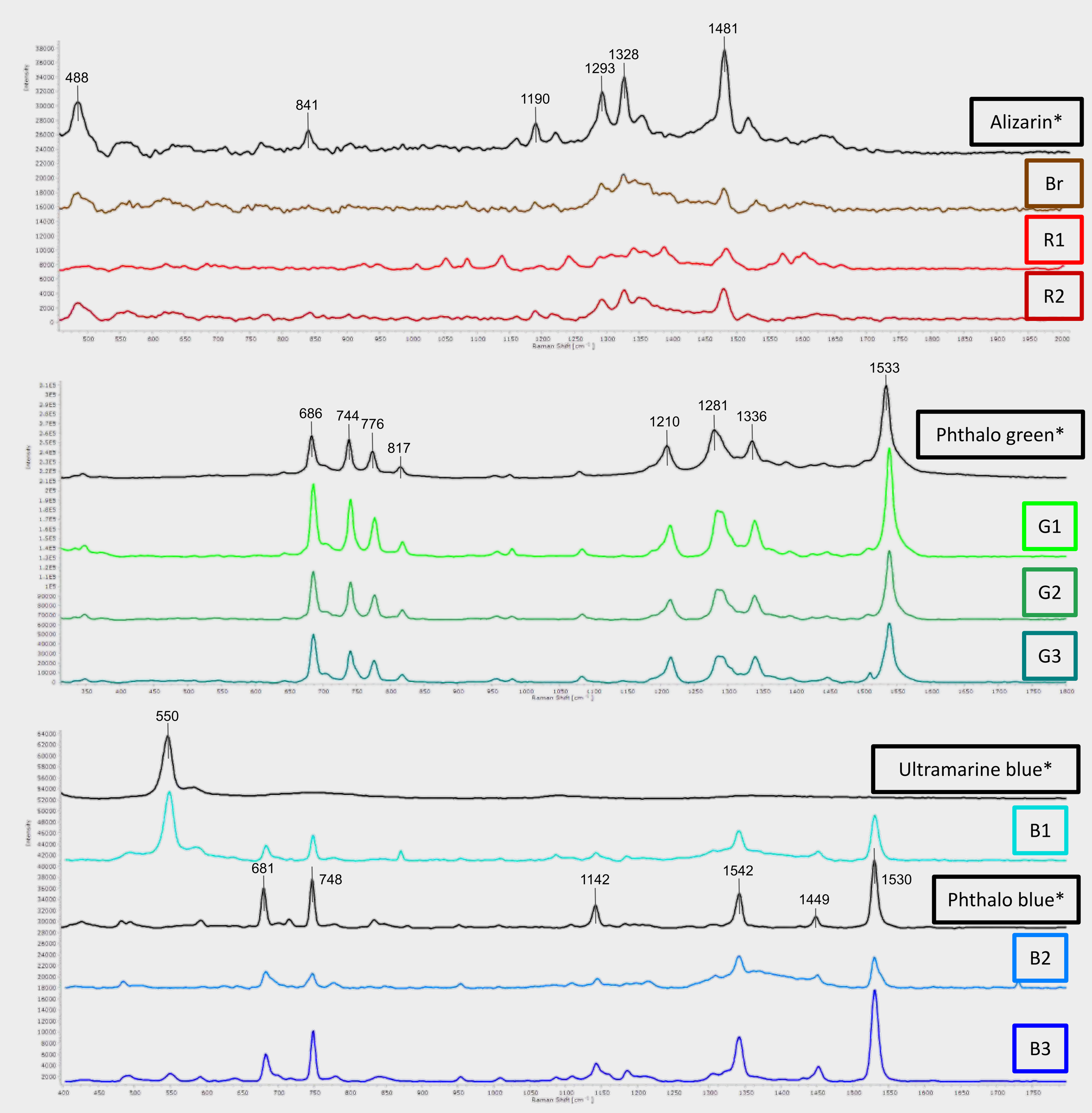

Fig.3 - Raman spectra (785nm) of selected samples from the paint palette compared with reference spectra of dry powdered pigment sourced from Kremer* (alizarin [23611], phthalo green [23002], ultramarine blue [45030] and phthalo blue [23070]).

Results & Discussion

The combination of MA-XRF and Raman spectroscopy has aided the identification of a range of synthetic inorganic and organic pigments from the paint palette (Table 1). The abundance of zinc detected throughout the palette and overlapping with areas of the SOPs, phthalo green and blue, is likely due to its presence in the form of a paint extender zinc oxide. Similarly, calcium is present in all three samples of reds and brown, likely in the form of substrate for the dye madder / alizarin. Within the same class of SOPs, a small variation of its chemical structure could result in a different pigment hue, as illustrated by the samples from the palette, where R2 and Br are in fact both alizarin, an anthraquinone dye, and several samples of green G1-3 exhibit various hues of phthalo greens and similarly for the B1-3 phthalo blues, both of which are phthalocyanines.

In the unsupervised machine learning model, the selected white, red and green endmembers mapping to specific areas of the painting correspond to the regions of titanium / zinc white, madder / alizarin and phthalo green of the paint palette, providing preliminary result on pigment identification.

Table 1 – Summary of the pigments identified from the selected regions of the paint palette. ‡Ultra-violet fluorescence image (not included herein) of the palette exhibited characteristic pinkish-orange fluorescence of natural madder (consists of purpurin or pseudopurpurin) in the region of R1, but not in the regions surrounding R2 and Br, which are likely to be alizarin, the synthetic form of madder.

	XRF	Raman	Pigment assignment
Brown (Br)	Calcium	Alizarin	Alizarin
Red (R1)	Calcium	Alizarin	Madder‡
Red (R2)	Calcium	Alizarin	Alizarin
Green (G1-3)	Copper, Zinc	Phthalo green	Copper phthalo green
Blue (B1)	Copper, Zinc	Ultramarine blue, Phthalo blue	Ultramarine blue, Copper phthalo blue
Blue (B2)	Cobalt, Zinc	Phthalo blue	*Cobalt phthalo blue (suspected)*
Blue (B3)	Copper, Zinc	Phthalo blue	Copper phthalo blue
Yellow (Y1-2)	Cadmium	—	Cadmium yellow
White (W)	Titanium, Zinc	—	Titanium white, Zinc white
Purple (P)	Cobalt	—	*Cobalt violet (suspected)*

Conclusion & Future work

This study has demonstrated the potential of an integrated technological approach by launching an extensive study on the artist's paint palette (or leftover artist materials), to establish the basis of a paint reference library of the artist to support further studies of the artist's paintings via unsupervised learning model UMAP of VNIR data. In this approach, VNIR data could be collected on paintings in one scanning session and then processed with a reference library by machine learning to provide preliminary results on the pigments present. With the non-invasive nature of data collection and upon building a more extensive reference library of artist material in future work, it is anticipated that the subsequent processing via machine learning model would continue to improve the efficiency of artist material identification.

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