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Intelligent Workflow for Real Time and Automated Analysis of Historical Pigments

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***Abstract* – In archaeological and conservation contexts, rapid and reliable access to information on painting materials is essential. To address this requirement, a completely automated system has been developed, combining data from Raman spectroscopy, spectrophotometry, and colorimetry, acquired on a set of 100 historical pigments from the ©Kremer Pigmente collection. After collecting the spectral data, which included a preliminary study to find the best settings and conditions for each measurement, the analysis workflow involved signal smoothing, baseline correction, identifying key features of each pigment, and data processing through custom Python pipelines. Raman, spectrophotometry, and colorimetric techniques contribute complementary molecular and chromatic information, enabling non-invasive diagnostics of polychrome materials. Automation dramatically reduces processing time compared to traditional manual analysis. This method offers a robust and transferable solution for the spectral documentation and recognition of pigments, providing immediate feedback on the pigment being examined and enhancing responsiveness in conservation and archaeological fieldwork.**

I. INTRODUCTION

The analysis of pigments in works of art plays a central role in art-historical interpretation, in the detection of potential forgeries, and in the development of strategies for restoration and preventive conservation. Accurate identification of painting materials is essential both for the scientific study of the artifact and for the planning of conservation interventions based on objective evidence.

Over time, pigments may undergo alteration or degradation processes that affect their original appearance, compromising the chromatic legibility of the artwork. Reliable characterization enables the reconstruction of the authentic pigments used during execution, providing a robust foundation for conscious conservation decisions and for the implementation of preventive measures aimed at slowing deterioration [1].

In this context, the conservation of polychrome artworks requires analytical methodologies capable of returning accurate and detailed information while minimizing the risk of damage to the artifact. Non-invasive diagnostic techniques - particularly those applicable in situ using portable instrumentation - represent an effective solution for rapid, adaptive, and sustainable investigations. Among the most widely adopted methods, visible-range diffuse reflectance spectrometry (vis-RS) and portable Raman spectroscopy have proven to be essential tools for the characterization of pictorial materials [2].

Vis-RS has become a reference technique in the study of cultural heritage materials due to its ability to discriminate between organic and inorganic compounds, monitor color alterations, and evaluate the effectiveness of conservation treatments such as consolidants, protective agents, and cleaning products. The reflectance spectrum of a pigment is strongly affected by physical and optical parameters such as particle size, dispersion medium, and refractive index. The ability to collect data from highly localized surface areas, combined with the simplicity, portability, and cost-effectiveness of the instrumentation, makes vis-RS particularly well-suited for the characterization of pure pigments under real-world conditions [2].

Raman spectroscopy, in parallel, is a fundamental technique for the molecular characterization of pigments in paintings, ceramics, manuscripts, and mural surfaces.

However, the presence of organic binders often generates strong background fluorescence, which can mask the Raman signal and complicate identification. Although portable Raman instruments do not achieve the same resolution and signal-to-noise ratio as benchtop systems, their capacity to analyze immovable or fragile artifacts makes them indispensable in on-site diagnostic campaigns [1].

Identifying the spectral fingerprint of a pigment remains a challenging task, particularly in the presence of degradation or complex mixtures. To ensure reliable outcomes, spectral analysis must be complemented by systematic and rigorous comparison with validated reference dataset, enabling objective and reproducible results.

One of the most critical challenges in this context is the ability to accurately recognize pictorial materials directly in situ, without relying on preliminary assumptions or engaging in time-consuming post-processing. Traditional methods involve a fully manual workflow [3]: each spectrum must be processed individually, the baseline corrected, diagnostic peaks identified, and the data interpreted by comparing it with values reported in the literature. This approach demands specialized expertise, is labor-intensive, and introduces interpretive variability, delaying the understanding of the materials under investigation.

To overcome these limitations, this study presents a fully automated workflow for the spectral analysis of historical pigments [4]. The system integrates Raman spectroscopy, spectrophotometry, and colorimetry and was designed to process raw spectral data through standardized and unsupervised pipelines. All stages of the analysis, including smoothing, baseline correction [5], peak detection, and features extraction (colorimetric and vibrational), are performed automatically through custom Python scripts. This approach provides immediate qualitative feedback without requiring any prior classification, assumptions or user intervention. Unlike static databases [6] that require manual searches, this system offers a dynamic and user-friendly solution for on-site diagnostics.

The proposed method was applied to a large set of historical powder pigments from the ©Kremer Pigmente collection, prepared following traditional recipes. Through the integrated use of Raman spectroscopy, spectrophotometry, and colorimetry, the system simultaneously extracts molecular information (Raman bands), chromatic parameters (L, a*, b*, C*, and h°), and spectral features, such as absolute and relative maxima from the first derivative of the Spectral Reflectance Factor (d(SRF%)). This combined approach providing an integrated and reliable characterization of the analyzed materials in just a few seconds.

II. MATERIALS AND METHODS

A. Historical pigments used for reference dataset

The reference set employed in this study comprises 100 historical pigments in powder form, each supplied in 3 mL containers by ©Kremer Pigmente (Germany). The samples were analyzed without any additional treatment or preparation. The collection includes materials traditionally used in historical painting, covering a broad chromatic range and representative of both organic and inorganic classes. As shown in *Fig. 1.*, all pigments were examined in their pure powdered state, without the addition of binders or extenders.

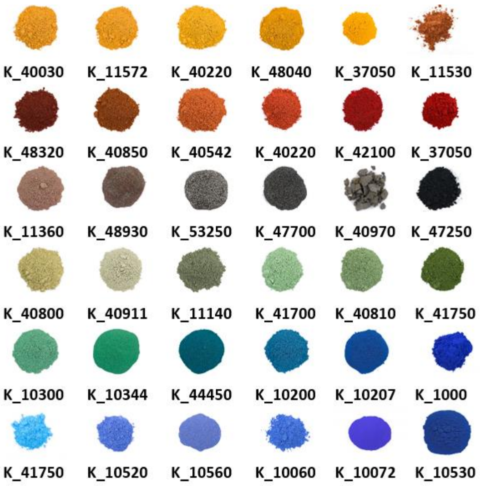

Fig. 1. Representative historical pigments from the ©Kremer collection, identified by their original producer codes.

B. Visible Reflectance Spectrometry (Vis-RS) Measurements

Vis-RS measurements were performed using a Konica Minolta® CM-2600d spectrophotometer (Konica Minolta, Tokyo, Japan), operating in the 360–740 nm range with a 10 nm acquisition interval. The d/8° geometry was adopted with a 28.26 mm^2 measurement area. Illumination was provided by a xenon lamp through an integrating sphere, ensuring uniform light distribution. A white calibration plate (CM-A145) and a black reference box (CM-A32) were used to adjust the reflectance scale [2]. Data were acquired in specular component excluded with ultraviolet contribution excluded.

C. Raman Measurements

Raman spectra were acquired using two different portable systems operating at 785 nm and 532 nm, respectively.

The first instrument was a portable modular system comprising a BTC162E Glacier® T spectrometer (B&W TEK Inc., Newark, DE, USA), a 785 nm FC-D-785 diode laser (CNI, Changchun, China), and a fiber-optic laboratory probe. The system featured a maximum laser power of 350 mW and a thermoelectrically cooled CCD linear detector.

A second Raman system, based on a BWS465-532S spectrometer (B&W Tek, Inc., Newark, DE, USA), was used for selected samples exhibiting weak Raman signals or strong fluorescence under 785 nm excitation. This instrument employs a 532 nm excitation laser, delivering an output power of 40 mW at the probe and is equipped with a high quantum efficiency CCD detector.

For both instruments laser power was adjusted depending on the sample, to avoid thermal damage and ensure good signal-to-noise ratio. The laser spot size was

85 µm at a 5.5 mm working distance. Spectra were collected in the 60–3000 cm^{-1} range, with variable integration times and ~5 cm^{-1} nominal resolution. Multiple scans were averaged to enhance spectral quality.

D. System Workflow and Data Processing Pipelines

The system developed in this study is built around fully automated pipelines for the analysis of historical pigments, integrating both spectrophotometry and Raman spectroscopy. As shown in *Fig.2.*, the architecture is designed to process raw spectral data through an intelligent sequence of Python-based scripts, providing immediate feedback and minimizing the need for manual data processing.

During the acquisition phase, which included a preliminary study to find the best settings and conditions for each measurement, spectral data were acquired on 100 reference pigments from the ©Kremer Pigmente collection. The input datasets included:

-*SRF% vs. wavelength* curves from spectrophotometry;

-Relative intensity vs. Raman shift curves from Raman spectroscopy;

-*Counts vs. energy* from X-ray fluorescence (XRF) as future integration.

Each dataset is automatically processed through a dedicated Python script:

-“*Lab1976.py*” performs colorimetric data using spectral reflectance data (SRF%), D65 standard illuminant and 10° standard observer. The script computes the tristimulus values (X, Y, Z) and subsequently derives the CIELAB coordinates (L*, a*, b*). From these, are calculate the chromaticity-related values: chroma (C*) and hue angle (h°).

-“*DP.py*” processes the raw data of SRF% to extract distinctive features of reflectance curves of each pigment. The script first applies Savitzky-Golay smoothing to reduce noise while preserving curve structure, then computes the first derivative of the smoothed curve to identify spectral extrema, such as maxima points, which are diagnostic of the pigment’s reflectance behavior. These features support pigment discrimination based on the shape and trend of the reflectance spectrum.

-“*Raman.py*” handles the preprocessing and analysis of Raman spectral data through a fully automated sequence customized for pigment characterization. Initially, it applies baseline correction using the Asymmetric Least Squares (ALS) algorithm [5], which effectively removes fluorescence-induced background while preserving the integrity of the Raman peaks. Subsequently, the script employs Savitzky-Golay filtering to smooth the spectra, reducing noise without distorting the signal. For peak detection, the script computes the first derivative of the smoothed spectrum and identifies maxima as zero-crossings where the derivative shifts from positive to negative. A minimum variation threshold is applied to the derivative to discriminate true peaks from noise-induced fluctuations, ensuring that only significant Raman features are preserved. This strategy ensures the robust extraction of diagnostically relevant Raman peaks, which act as molecular fingerprints for pigment identification.

The outputs of each Python script are stored in structured data files forming a reference dataset. A dedicated interface script manages the automated execution of data processing scripts and enables the visualization of results. This multi-input approach will improve the reliability of the identification process of unknown samples and enable their reliable and fast recognition. The system’s immediate feedback capability and standardized workflow make it particularly well-suited for dynamic operational contexts such as restoration sites, archaeological excavations, or museum environments.

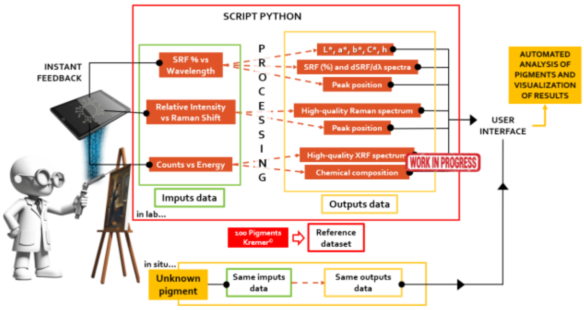

Fig. 2. Functional diagram of the automated system for the analysis of historical pigments.

III. RESULTS AND DISCUSSION

The system's performance was thoroughly assessed by applying the automated processing pipelines to a reference dataset consisting of 100 historical powder pigments from the ©Kremer Pigmente collection. As outlined in the previous sections, each pigment was characterized using both spectrophotometry and Raman spectroscopy, and the resulting data processed through the respective analysis scripts.

The system demonstrated high reliability in extracting meaningful spectral features across the entire dataset. In the case of SRF% data, it successfully captured the characteristic reflectance behavior of each pigment, automatically identifying key maxima from the first derivative of the curve. As shown in *Fig. 3.*, pigments such as K_40320 (Dark Ochre) displayed well-defined peaks centered around 580 nm, corresponding to the typical spectral behavior of iron oxide-based earth pigments. Similarly, K_17400 (Cipro Green Earth) exhibited complex reflectance profiles with multiple extremal points detected between 430 and 520 nm, highlighting the system’s sensitivity to subtle chromatic transitions. The accurate detection of these features confirms the robustness of derivative-based analysis and its ability to support pigment identification through spectral morphology alone.

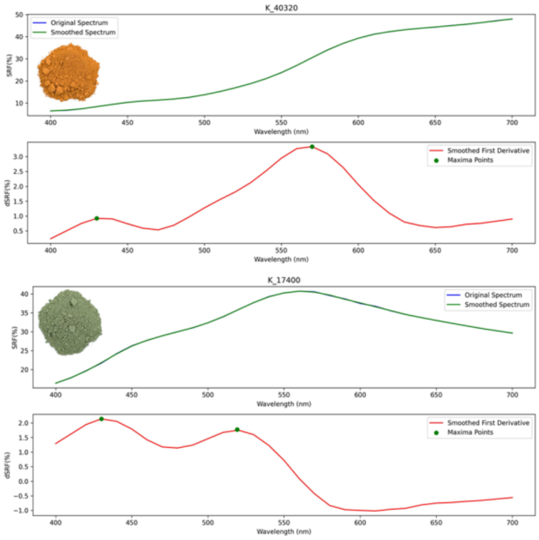

Fig. 3. SRF(%) and first derivative of SRF(%) for four reference pigments: K_40320 (Dark Ochre), and K_17400 (Cipro Green Earth). The plots show the smoothed reflectance spectra (green curves) and the first derivative with automatically detected maxima (red curves).

In Raman spectra, the system successfully identified vibrational features relevant for pigment characterization, even in the presence of varying levels of fluorescence and noise. Peak detection was performed by analyzing the first derivative of the smoothed spectrum and isolating maxima where the derivative variation exceeded a defined threshold, allowing for the identification of meaningful peaks while minimizing false positives. The number and sharpness of detected peaks varied depending on the pigment's molecular structure and signal intensity. As shown in *Fig. 4.*, K_10620 (Cinnabar) exhibited three strong and well-defined Raman peaks in the lower Raman shift region, typical of mercury sulfide-based pigments. K_48944 (Micaceous iron oxide) showed a large, less structured spectrum with lower signal intensity, yet the system was still able to extract several meaningful maxima, demonstrating its robustness even with weakly scattering or amorphous materials. These results confirm that the system can adaptively extract spectral features across a variety of Raman profiles without operator intervention. The ability to consistently detect and localize vibrational bands, regardless of signal complexity, supports the method's effectiveness in building reliable spectral fingerprints for use in pigment identification.

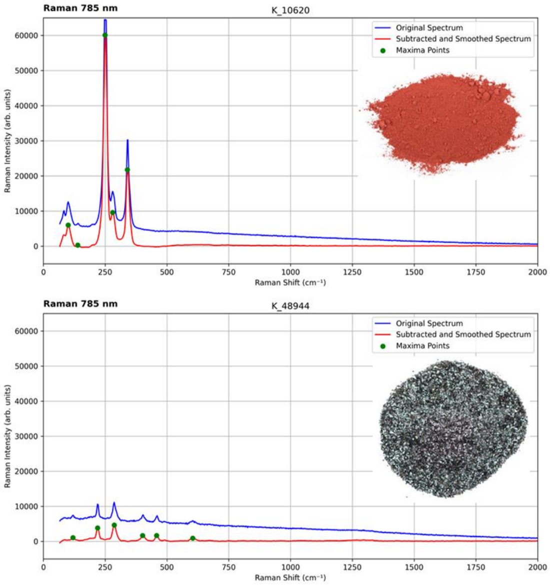

Fig. 4. Automated Raman spectral processing for three reference pigments: K_10620 (Cinnabar), and K_48944 (Micaceous iron oxide). Each plot shows the original spectrum (blue), the baseline-subtracted and smoothed spectrum (red), and the automatically detected maxima (green spots).

IV. CONCLUSIONS

This work proposes the development of an intelligent and fully automated system for the spectral analysis and identification of historical pigments through non-invasive techniques, such as Raman spectroscopy and spectrophotometry. The optimized workflow begins after spectral data collection, ensuring that all procedures - smoothing, baseline correction, features extraction, and comparison - are handled automatically via custom Python pipelines with minimal operator intervention. A key strength of this system lies in its extremely rapid processing time: the entire analysis, from raw data to output results, is completed in a matter of seconds per sample. This makes it particularly suitable for dynamic operational contexts such as in situ diagnostics, conservation sites, and archaeological investigations.

Future developments will extend the system's capabilities by incorporating automated pipelines for X-ray fluorescence (XRF), further enhancing the compositional analysis of pigments.

This work represents one of the core objectives of the MUR-PNRR "SiciliAn Micro and nanO TecHnology Research And innovation CEnter" (SAMOTHRACE) - Work Pillar Cultural Heritage project, which aims to develop intelligent tools that support researchers in the analysis of materials and in solving problems related to archaeology and the conservation of historical and artistic heritage.

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