Statistical analysis of laser-based spectroscopic data elucidates painting materials

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Combining multivariate statistical analysis, Raman spectroscopy, and laser-induced breakdown spectroscopy helps to identify and classify the material constituents of artworks.

The analysis and discrimination of painting materials (such as pigments, binding media, varnish, and composite materials like alloys and ceramics) is critical to establishing the origin and value of the art and artifacts that contribute to cultural heritage. But analysis is also complex because of the vast range of inorganic and organic compounds found in paintings. The need for portable instrumentation for investigating art and artifacts has spurred interest among scientists in constructing appropriate new devices for studying complex materials. These devices in turn have led to the development of novel laser-based instrumental methods for investigating and monitoring changes in the condition or degradation of artworks. However, we still face challenges regarding in situ system implementation and interpretation of results. Moreover, integrating the efforts of engineers and analytical scientists is crucial for optimizing the entire research endeavor. To this end, mathematical analysis of complex spectral data has proved very useful for classifying data.

Raman spectroscopy and laser-induced breakdown (LIB) spectroscopy (also known as laser-induced plasma spectroscopy) have been used to analyze paint\(^2,3\) and other materials,\(^4,5\) providing complementary molecular and atomic information that enables identification of original and nonoriginal materials in works of art. Subsequently applying statistical methods to the spectra makes it possible to classify samples.\(^6,7\) Raman and LIB spectroscopy are usually performed using a variety of instruments equipped with different optics and lasers.\(^3\) We recently built a combined setup capable of acquiring both types of spectra.\(^2,6\) Detecting weak Raman signals (from pigments) often necessitates working in the dark with a continuous laser source, whereas a pulsed laser is needed to generate a plasma for LIB spectroscopy. Operating in darkness is possible in the laboratory but complicated when working directly on paintings and monuments.

Our approach focuses on engineering a compact, combined instrument based on second-harmonic (532nm) emission of a pulsed nanosecond Nd:YAG (neodymium-doped yttrium aluminum garnet) laser, an intensified gated detector, and suitable optics (see Figure 1). A key aspect of this approach is to assure controlled ablation of material in LIB spectroscopy, and the collection of sufficient Raman signal from the same spot using the same laser source, monochromator, and detector. We have explored statistical analysis of recorded spectra using databases of reference materials and multivariate statistical analysis of groups of spectra following the selection of suitable regions of interest in the Raman or LIB spectra (based on the position of atomic emission lines or specific vibrations).

We tested the instrument on synthetic and natural ultramarine pigments, which are characterized by different trace materials.\(^8\) In addition, we combined depth profiling of multilayered samples using ablation (LIB spectroscopy) followed
by the acquisition of Raman spectra.\textsuperscript{2,9} We encountered challenges in the interpretation of differences in spectra from similar materials. Consequently, we aimed to classify the data (associated with only small differences in Raman or LIB spectra) using multivariate analysis.

Ultramarine is a mineral pigment based on lazurite (the blue component of lapis lazuli). Historically, it was one of the most expensive pigments. The analysis of ultramarine samples using the combined approach allowed both rapid identification of the pigment through the presence of characteristic vibrational bands in the Raman spectra and differentiation of samples based on the presence of specific elements—i.e., calcium, sodium, aluminum, and magnesium—by LIB spectroscopy (see Figure 2: magnesium not shown). We analyzed a group of LIB spectra of different pigment samples using principal component analysis (PCA), which enables separation of artificial and natural materials (see Figure 3). We probed a 50–100\textmu m area of the sample using a so-called macro-Raman analyzer. The resulting spectra indicated the presence of the trace minerals calcite and silicate (i.e., diopside and wollastonite), impurities only found in samples of natural origin.

In other applications, such as analysis of corroded gilded bronze, wall paintings, and glass mosaic tesserae from the Renaissance, as well as layered samples of mixed polymers used in conservation, the combined approach has enabled depth-profiling of complex materials with different surface and bulk composition.\textsuperscript{2,9} Each laser pulse removes material, and Raman and LIB spectra are recorded at increasing depths. Moreover, the analysis of painting materials using micro- and non-destructive methods continues to advance. It has been extended to the analysis of other conservation polymers using both PCA and alternative chemometric prediction methods,\textsuperscript{10} as well as analysis of other pigments in artworks.\textsuperscript{11}

In summary, the integration of LIB and Raman spectroscopies is promising for the analysis of materials found in cultural art and artifacts, offering complementary information that can inform sampling strategies for more specific investigation. Using statistical methods greatly improves the classification of Raman and LIB spectra, and highlights key differences in materials. But it is still necessary to interpret these differences with reference to specific chemical or physical phenomena. In future, we plan other applications involving the integration of Raman and LIB spectroscopies with additional analytical techniques, including time-resolved laser-induced fluorescence.
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References