A112 Development of a Pigment Classification Scheme by Raman Spectroscopy

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After attending this presentation, attendees will understand a broad overview of the development of a procedure for systematically identifying pigments in samples of forensic interest by Raman spectroscopy.

This presentation will impact the forensic science community by understanding how pigments in paint are overlooked in paint evaluation samples. The presentation will discuss results of several years of research on pigment identification. The presentation will also present a scheme for approaching and conducting pigment identification.

Colorants (pigments and dyes) are everywhere. In theory, they seem like an obvious material to exploit as forensic evidence; yet beyond the macroscopic color that colorants impart to a material, the identity of individual pigments or dyes are largely ignored in forensic casework. The reason for this is the small size and low relative concentration of pigments in a given application. Successful efforts have been made to characterize select pigments in specific forensic applications (by XRF, FTIR, PLM and microchemistry, for example); however, each of these approaches has been subject to a particular limitation that has prevented the widespread application of pigment evidence to forensic investigations.

The development of Raman microspectroscopy has opened a new avenue for the possibility of identifying pigments in a consistent and reliable manner. The art community has embraced this technology and has made great strides in developing Raman spectroscopy as a practical analytical tool for pigment identification; however, the requirements of the art and conservation disciplines differ somewhat from those of the forensic laboratory. To this end, a program of research in the analysis of pigments by Raman spectroscopy with the aim of developing a practical approach for forensic scientists to exploit pigment evidence in casework has been conducted. These results have applications for both comparative forensic examinations as well as developing investigative leads, the latter of which could assist with sourcing paint samples.

In this research, samples were selected from a physical pigment reference collection of over 1,100 pigments. Samples were selected to represent as many organic and inorganic pigments as possible. When multiple samples of a given pigment existed, samples with stronger provenance were selected. Each pigment sample was analyzed by Raman spectroscopy, under varying conditions to obtain the best possible spectrum. In total, over 250 different pigments were examined and a database of Raman spectra was established.

Due to the fact that pigment samples are not always uniformly named by manufacturers (despite Colour Index naming conventions) and that samples have varying provenance, pigment identity was verified by several orthogonal methods. For example, Raman spectra were checked for consistency by comparing to other samples of the same pigment. Spectra were also compared to other chemically related pigments to ensure that chemically related pigments were spectroscopically related. All pigments were also elementally analyzed to ensure that the elemental data was qualitatively consistent with published compositions. Pigments with varying polymorphs were verified or identified by powder x-ray diffraction. Ultimately, any impure pigments or those with conflicting data that could not be resolved were withdrawn from the collection.

The Colour Index, maintained by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists, provides a basic level of chemical grouping in there classification approach; however, it was established that the chemical groups specified by the Colour Index were not sufficient in scope to provide the level of classification necessary to take advantage of the level of data in a Raman spectrum. As such, a new program of chemical groups was devised (drawing from many literature sources, as well as our own knowledge) that was consistent with the spectroscopic data. Major peaks from the pigment reference spectra were then used to spectrally sort pigments into the defined chemical groups. The result was the development of a forensic pigment identification scheme that permits identification of the majority of pigments in modern commercial use through a flow-chart type approach. The scheme is expandable to accommodate other pigments that are not currently in the collection. Pigments with strong fluorescence obviously cannot be grouped by this method; however, they are included in the appropriate chemical group.

Ultimately, this identification scheme permits specific identification of pigments (when possible), but also allows an examiner to determine the extent to which a pigment can be identified or grouped. For example, pigments within certain chemical groups have indistinguishable Raman spectra, which mean that a pigment can only be identified to a certain level (e.g., certain diarylide pigments). In other cases, pigments can be identified as a single specific pigment. The benefits of such an identification scheme will be illustrated through the analysis of a small group of paint samples.

Pigment, Raman Spectroscopy, Paint