A115 Systematic *In Situ* Identification of Pigments in Paint by Raman Microspectroscopy

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The goal of this presentation is to demonstrate ways in which Raman spectroscopy can be incorporated in a forensic laboratory to improve the evidentiary significance of paint evidence.

This presentation will impact the forensic science community by suggesting the first systematic organization of pigment analysis that is broadly applicable to forensic paint analysis.

Colorants (pigments and dyes) surround us in everyday life, yet beyond spectrophotometric comparisons of bulk color, forensic analyses typically ignore the colorants within a sample. This is due in large part to the fact that colorants are present at low concentrations, and pigments are, in addition, typically quite small (<1µm), making them difficult to access analytically. Successes have been achieved through a number of microanalytical methods, including polarized light microscopy, infrared microspectroscopy, microchemistry, micro x-ray fluorescence, and X-ray diffraction; however, the application of each of these approaches is limited by one or more factors such as analytical volume, specificity, sample preparation requirements, or the level of interpretation expertise required.

Raman microspectroscopy suffers from two of its own major limitations, which are fluorescence and the current lack of a systematic approach to pigment identification. Fluorescence can be minimized through the use of multiple laser wavelengths, photo bleaching, and background removal, yet it remains the Achilles heel of the technique, leaving some pigment spectra inaccessible by this method. The second issue, regarding interpretation, is being reduced by the fact that more and more laboratories are obtaining and using Raman systems; however, the framework for analyzing and interpreting paint evidence remains limited. This presentation, whose primary focus is to address this shortcoming, will provide an overview of our past six years of research, which has focused on the development of: (1) a pigment identification scheme; (2) laboratory methods designed to optimize pigment analysis; and, (3) of interpretation and significance studies that will provide a framework for assessing the value and uses of pigment information.

Through the development of an extensive database of pigments (>1,100 pigments and >325 unique pigments), a classification scheme for the systematic identification of pigments was devised. Each pigment in this database has been carefully verified by orthogonal methods and categorized by chemical structure. The Raman spectra and pigment chemistry have been used together to develop a flowchart that permits classification of pigments on the basis of strong peaks, which is intended to be applicable at the bench level. Within the context of an investigation, it also permits an examiner to determine which pigments can (and can't) be discriminated on the basis of strong peaks in a sample spectrum. This organization provides the first systematic basis for addressing pigment identification in forensic-sized samples. It also shows that of the 325 unique pigments studied, only 38 (~12%) had strong enough fluorescence that no useful Raman scattering was observed (using 514 and 785nm lasers).

Building upon this identification scheme, the second phase of this research focused on the *in situ* identification of pigments in paint, with a goal of systematically addressing the evidentiary significance of pigment identification within a polymer matrix. Various methods of sample preparation and interpretation were evaluated to determine whether any methods are optimal. The analysis focused on a collection of 300+ late model automobile paint samples (comprising over 1,000 paint layers) and several sets of architectural tinting pigments (used to color the majority of architectural paints in the U.S.) collected over recent years. The color layers in all of these paints (over 500 layers), which included top coats, tinted clear coats, and coordinated primers, as thin as 5µm in cross section, were analyzed by micro-Raman spectroscopy to identify the pigments present. In total, 28 different pigment groups were identified among the automotive paints and 14 pigments were identified within the architectural tinting colors. Paint pairs from the automotive paint collection of the same color code were also characterized by micro-FTIR spectroscopy. These results were interpreted to evaluate the potential applications of Raman spectroscopy in a trace evidence lab, with a specific focus on evaluation of the method as: (1) a fast screening method (for with no preparation); (2) to provide additional discrimination in conjunction with existing micro-analytical methods; and, (3) as a method to provide manufacturer sourcing assistance based on the identification of specific pigments. Each of these applications will be expanded upon in the presentation.

Paint, Pigments, Raman Spectroscopy

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