



A116 Classification of Organic Pigments by Raman Spectroscopy

Christopher S. Palenik, PhD*, Bryn M. Wilke, AS, and Skip Palenik, BS, Microtrace, 790 Fletcher Drive, Suite 106, Elgin, IL 60123-4755

The goal of this presentation is to follow up on previous seminars regarding the study of pigments by Raman micro spectroscopy with an emphasis on forensic applications.

This presentation will impact the forensic science community by presenting the first general classification of organic pigments.

Pigments are encountered in a variety of trace evidence, including automotive paints, architectural paints, inks, fibers, and other polymers of many varieties. Traditionally, pigments have been studied by polarized light microscopy, microchemistry, infrared spectroscopy, pyrolysis GC/MS, SEM/EDS and X-ray diffraction. Limitations inherent to each of these techniques have limited the practicality of pigment identification in the analysis of trace evidence. Raman spectroscopy, which is slowly becoming a more common instrument in forensic laboratories, provides the spatial resolution and sensitivity to pigments (over binders and other fillers) necessary for their effective and reliable characterization and identification.

Over the past three years, the utility of Raman spectroscopy as a technique for identifying both pigments in their free form and *in situ* in architectural and automotive paints has been demonstrated (Palenik et al., 2007, Palenik et al., 2008). During this period, a Raman spectral library of approximately 200 different pigments has been established. This includes most major automotive and architectural pigments.

With the development of this Raman database and evidence supporting the ability to identify pigments *in situ*, several higher level questions begin to arise. This presentation addresses several of these questions, which include:

Are the Raman spectra from a given pigment reproducible? Given the difficulty of obtaining pigment samples, how reliable are the samples in a given collection? Are pigments produced under the same chemical index number by different manufacturers consistent with each other or can they be differentiated. Finally, and most significantly, to what extent can a given pigment be specifically identified by Raman spectroscopy (to chemical class or to the actual pigment name)?

Results to date show multiple spectra collected on different days from the same pigment and from different pigment particles in the same sample are reproducible. More specifically, the wavenumber shift of major, medium and minor intensity peaks (peaks >5% intensity relative to the maximum peak) is reproducible.

In regards to the question of manufacturer to manufacturer variability, analysis of modern pigments purported to be of the same chemical index produced by different manufacturers have each been found to be spectroscopically consistent with each other, even when produced under different trade names (to date). The only exception identified to date is a historic artist's pigment with a questionable chemistry that has been produced in different (and disputable) ways over the years (Indian yellow pigment).

With the above supporting background, the ultimate question regarding pigment characterization can be addressed: the extent to which various pigments can be differentiated by Raman spectroscopy. Just as animals can be grouped by genus and species, pigments can be grouped into a general chemical class (e.g., diarylide yellow, diazo, phthalocyanine, etc.) and then more specifically identified by specific R- groups. By characterizing multiple pigments in the major general pigment classes, the extent to which specific pigments can be differentiated will be discussed. For example, the study of multiple pigments from a single class has shown that pigment classes can generally be identified on the presence of certain groups of bands. This is somewhat analogous to the ways in which functional groups can be recognized in the infrared by characteristic peak positions and shapes. More specific pigment identification can, in most cases, be made by examining the finer details of the Raman spectrum. In some cases; however, it was not possible to differentiate between certain pigments by Raman spectroscopy alone. The result of this work is the first iteration of a pigment identification scheme that relies upon grouping of pigments by chemical class rather than being reliant upon a spectral library search to identify pigments. The advantage of this development is the potential to obtain useful chemical information from the Raman spectrum of a pigment that has not been previously characterized or included a spectral database.

Pigment, Raman, Microscopy