B139 An Introduction to the In Situ Identification of Pigments in Automobile and Architectural Paints by Raman Microspectroscopy

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The goal of this presentation is to introduce the audience to raman spectroscopy and its use in identifying pigments in automotive and architectural paints.

Though a critical part of automobile finish systems and other paints, pigments are generally not critically examined in forensic analyses. This presentation will impact the forensic science community by demonstrating a means by which pigments can be effectively and efficiently studied.

Despite the significance of automotive and architectural paint in the field of trace evidence, only two of the three major components of paints (*i.e.*, binders and extenders) are presently reliably identifiable in microscopic specimens. Pigments, the third major component of paints, are only indirectly used as a discriminating factor through the study of the composite color they produce by visual examination or visible microspectrophotometry. The identity of the actual microscopic particles responsible for the macroscopic color of paint are generally ignored. In large part, this is due to the difficulty of studying and identifying pigments by methods commonly available in forensic laboratories. Polarized light microscopy and x-ray diffraction can be used to identify pigments, but, these methods are not commonly utilized due to the expertise required or the amount of available sample. A pyrolysis gas chromatogram may contain information about the pigments present; however, this information typically is not used to identify pigments but instead characterize and compare samples. Infrared spectroscopy can be used to identify certain pigments; however, the majority of peaks due to pigments are typically obscured by binder absorptions in the infrared. Raman spectroscopy, on the other hand, is normally free of scattering from the binder and often provides a great deal of information about the pigments present.

As a complimentary technique to IR, Raman spectroscopy is well suited to the examination of pigments. First, modes that are infrared active are generally inactive in the Raman spectrum. As a result, the paint binder does not usually interfere with the pigment spectrum and pigments typically show strong Raman scattering. Second, pigments in paint can be examined with virtually no sample preparation (the study of minor pigment components does require a thin sample). Third, although the detection limit within a measured sample volume are not particularly good (~5-10%, similar to other vibrational spectroscopies) compared to many other methods (e.g., ICP or XRF); microscopic and sub- microscopic pigment particles can be successfully studied individually by reducing the analysis volume using confocal Raman spectroscopy (down to ~2 μm^3).

Prior to the examination of pigments within a paint sample, it is necessary to develop a database of Raman pigments. At the present, our database consists of approximately 100 of the more commonly used commercial paint pigments. In collecting good Raman spectra, it was necessary to use two different lasers (514 nm and 785 nm) due to fluorescence that occurs in some pigments excited with a particular wavelength. Furthermore, background subtractions were often used to eliminate fluorescence backgrounds and improve the effectiveness of database search algorithms.

After building our Raman pigment database, we began to analyze various architectural and automotive paints. A series of six different colored acrylic architectural paint samples (white, gray, blue, green, black, and red) were examined by X-ray diffraction to identify the pigments they contained. These same samples were then characterized by Raman microspectroscopy. All of the pigments identified by X-ray diffraction were also identified by Raman spectroscopy. In addition, two different phthaolcyanine pigments used in the blue and green paint that were not identified in the XRD patterns were readily identified by Raman spectroscopy.

In this study of automobile paints, one to two pigments in a given sample without any background information concerning the pigments used in a given formulation have been routinely and blindly identified.

Several difficulties did arise in the identification of pigments in a given paint sample. One inherent problem relates to the scattering efficiencies of various pigments. For example, phthalocyanines, which are excellent Raman scatterers can dominate a spectrum if present even in a low concentration. In other cases, pigments present only in minor amounts can be difficult to study due to the difficulty of obtaining a clean Raman spectrum. This is not always the case and we have been encouraged to find that, in several cases, we could identify individual pigments present within a matrix of another pigment using a combination of light microscopy and confocal Raman spectroscopy. In general, we have found that Raman spectroscopy is an effective and efficient techniques for the identification of pigments in paint samples.

Raman Spectroscopy, Pigments, Paint