D70 Discrimination of Dyed Fibers Using Raman Microspectroscopy for Forensic Analysis

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The goal of this presentation is to evaluate the potential of Raman microspectroscopy to discriminate between common fiber classes, fiber subclasses, and fiber dyes in a forensic setting.

This presentation will impact the forensic community and/or humanity by providing the ability to obtain discriminating Raman spectral data on mounted fibers, which will greatly improve the forensic scientist's capability to identify fibers that cannot be discriminated by other techniques or samples that cannot be re-mounted.

Fibers are commonly encountered as trace evidence in crimes involving personal contact, such as homicide, assault, or sexual offenses. The value of these fibers as evidence depends on the forensic scientist's ability to identify and discriminate different fibers. Typically, fibers are visually identified using polarized light microscopy (PLM), however various spectroscopic methods (*e.g.*, UV-Vis, IR and Raman) have also been shown to be useful for fiber discrimination. Whereas PLM provides morphological and index of refraction information, spectroscopic measurements can provide more direct molecular information and in the case of IR and Raman, unique vibrational "signatures" can be obtained. Raman spectroscopy can potentially be used to determine the generic fiber class (*e.g.*, cotton, acrylic, polyester, nylon), and gain information on the structures of the dyes present, without the need to remove the fiber from the mounting medium. In Raman analysis, the ability to use glass slides is a tremendous advantage compared to IR, where the fiber must be removed, and remounted in a cell that is IR compatible. A disadvantage of Raman spectroscopy is that the relatively weak Raman signal can become easily overwhelmed by high backgrounds from thermal degradation products or sample fluorescence. The effect of high background signals can be minimized by either reducing the background or increasing the relative intensity of the Raman signal. Raman signals can sometimes be increased substantially by the use of resonance Raman spectroscopy (RRS) or surface-enhanced Raman scattering (SERS) techniques. Raman signal enhancements from 10^5 to 10^6 are often reported using these techniques, and still larger enhancements can be realized using the two together (SERRS). Both techniques have been used to generate enhanced Raman signals for fiber dyes alone, as well as dyes on fibers.

A study evaluating the potential of Raman microspectroscopy to discriminate between common fiber classes, sub-classes and fiber dyes in a forensic setting will be presented. The Raman spectra show features from the base fiber, the dyes on the fiber, and other fiber constituents such as TiO_2, a delustering agent. The Raman spectra also show features due to mounting materials and so care must be taken in the selection of mounting adhesives, slides and cover slips.

Raman microspectroscopy is used to quantify TiO_2 levels in delustered polyamide fibers at concentrations from 0-7.1%. Issues of concern found in measurements of TiO_2 in textile fibers include particle spacing and the possibility of particle agglomeration, which can lead to large signal variations. Methods to alleviate this signal variation will be discussed. Depolarization ratios have also been measured for TiO_2 in polyamide fibers for the purpose of providing additional discriminating data. It was found that the depolarization ratios are affected by polarizing effects of the fibers themselves. Solutions to this issue will also be discussed.

Dye fluorescence can be a concern for many types due to the typically weak Raman signals. Also, degradation products can be produced by thermalor photo-degradation of fiber dyes and can contribute to high background signals. We have found that degradation product background signals can be minimized through careful control of the laser power incident on the sample. In general longer-wavelength laser excitation also reduces background signals by reducing both direct fluorescence and laserinduced dye degradation. It has also been found that SERS and RRS can be used for many types of fiber dyes to obtain greatly enhanced Raman signals. The use of SERS, RRS and SERRS is being explored to measure both extracted dyes and dyed fibers directly. SERS is also useful in suppressing fluorescence as the metal surfaces typically used for SERS quench fluorescence for adsorbed dye molecules. SERS and RRS data will be shown for both dyes and dyes on fibers.

The intent of this paper is to evaluate Raman microspectroscopy for the identification of fibers and dyes of forensic interest. Raman spectroscopy has great potential to contribute to the forensic analysis of textile fibers. The ability to obtain Raman spectra on mounted fibers will greatly improve the ability to identify fibers that cannot be discriminated by other techniques such as FT-IR or samples that cannot be re-mounted.

Fibers, Raman Microspectroscopy, SERS