A151 Forensic Characterization and Identification of Dyes Extracted From Millimeter-Length Fibers Using Ultra-Performance Liquid Chromatography/Mass Spectrometry

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The goal of this presentation is to communicate to the forensic community results from ongoing research on development and validation of methods for chemical characterization of dyes extracted from millimeter to sub-millimeter length trace evidence fibers.

This presentation will impact the forensic science community by using the working hypothesis that liquid chromatographic separation and detection of individual dye components by mass spectrometry (LC/MS) provides a qualitative and semi-quantitative fiber dye "fingerprint," with the prospect of enhancing discrimination for comparison of known and questioned casework fibers. Determining the number and relative amounts of dyes present, and characterizing those dyes at the molecular level by MS, offers an entirely new level of information that is not otherwise available from microscopic or spectroscopic methods. Such information may also open the possibility of tracing specific dye formulations to the textile manufacturer.

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The current work explores the application of ultra-performance liquid chromatography (UPLC) for analysis of dyes extracted from fibers. UPLC uses high pressures (>10,000psi), smaller column particles (<2μm), and short columns (~5cm) for high speed, resolution, and sensitivity. If sufficient fiber is available, UV/visible diode array detection may be suitable for rapid low cost screening of trace evidence samples by UPLC. With extractions from 10mm single fibers of nylon, acrylic, and polyester, the amounts of eight different corresponding acid, basic, and disperse dyes ranged from 5 to 20ng with standard deviations from 1 to 3ng. UV/visible detection limits are in the low ng range for dye extracts from 10mm fibers, although quality of absorbance spectra is compromised at lower lengths.

Liquid chromatography tandem mass spectrometry (LC/MS/MS) has been widely used in forensic toxicology due to its high sensitivity and selectivity. With tandem MS/MS with multiple reaction monitoring (MRM) of specific molecular ion-fragment ion transitions we have reliably detected extracted dye amounts as low as a few tenths of ng from commercial textile fibers as small as 0.5mm in length. For example, five 0.5mm length nylon fibers commercially dyed with three acid dyes resulted in the following mean extracted dye amounts and % relative standard deviations: C.I. Acid Yellow 49, 0.15 ± 0.02ng (13.22%); C.I. Acid Red 337, 0.36 ± 0.04ng (10.95%); and, C.I. Acid Blue 281, 0.19 ± 0.03ng (18.34%). Linear calibrations based on five concentration levels of dye standards produced coefficients of determination (R^2 values) ranging from 0983 to 0.999. A miniature guillotine for improving the reproducibly of cut fiber length was designed. However, the difficulty involved in cutting sub-mm fiber lengths reproducibly is the primary reason that percent relative standard deviations for extracted dye amounts from replicate 0.5 mm fibers is relatively high. Further LC/MS validation work and technology transfer is also in progress in collaboration with the Forensic Services Laboratory of the State Law Enforcement Division (SLED), Columbia, SC.

In summary, analysis of dye extracts from single acrylic, nylon, and polyester fibers of 0.5mm lengths has been achieved. In tandem MS, two or more stages of mass analysis are combined in one experiment. Each stage provides an added dimension in terms of specificity of structural information characteristic of the target analyte. Multiple reaction monitoring is a common LC/MS/MS detection mode in which pairs of target parent ions and unique fragment ions are used for quick and accurate identification of target analytes. MRM detection enables high discrimination between different dyes because transitions to a characteristic fragment ion are unique to the molecular structure of the parent ion. The specificity of analysis allows simultaneous identification and quantitation at exquisitely low detection limits (e.g., 0.1ng or less for acid dyes extracted from nylon). Using the collection of several hundred textile dyes in the laboratory, infusion of dye standards can establish an MRM transition library. Routine LC/MS/MS screening with an MRM library has the potential to provide unambiguous identification for those dyes. For dyes not in the library, MS/MS analysis can still provide discrimination based on molecular structure differences.

Trace Fiber Examination, Textile Dye Analysis, Liquid Chromatography/
Mass Spectrometry