A142 Validation of Liquid Chromatography Methods for Trace Analysis of Dyes Extracted From Acrylic, Cotton, Nylon, and Polyester Fibers Using UV/Visible and Mass Spectrometric Detection

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After attending this presentation, attendees will be knowledgeable about analytical methods for microextraction of dyes from trace evidence fibers. Dyes can then be identified by standard liquid chromatography with UV/Visible detection or structural characterization can be accomplished by mass spectrometry. Participants will also gain an understanding of the validation protocols which have been followed to document accuracy, precisions, and limits of detection.

This presentation will impact the forensic science community by demonstrating validated protocols for dye extraction from trace evidence fibers of 1mm. The profiling of dye formulations on trace fibers at parts-per-million (ppm) levels allows match exclusion conclusions to be made with higher reliability, and "results consistent with" will have increased probative significance.

Forensic fiber examinations involve comparison of trace evidence fibers to determine possible associations between victims, suspects, and crime scenes. Fiber evidence is class evidence; discovery of a fiber at a crime scene and its identification as a particular fiber type (e.g., acrylic, cotton, nylon, polyester) may not provide much support for a forensic investigation. What is required is information that makes the trace evidence more specific and discriminating. While fast nondestructive methods such as microscopy and UV/Visible microspectrophotometry or Infrared (IR) spectroscopy are preferred for forensic fiber examinations, these techniques do not always provide enough discriminative information to establish a common origin between fibers. The premise of ongoing research is that if dye formulations on trace fibers can be reliably profiled at trace levels, match exclusions can be made with higher reliability, and "results consistent with" will have increased significance. Population studies report that fibers at crime scenes can be as small as 2mm in length. Because extraction of dyes from a fiber is destructive to the evidence, it is desirable to analyze fibers in the mm or sub-mm range.

Fibers that are similar in visual appearance can often be discriminated by retention time matching and UV/Visible profile comparison without the need for Mass Spectrometry (MS). The use of tandem mass spectrometry offers provides sensitivity and unequivocal structural identification of the dye components. Separation and detection of individual dye components provides a qualitative and semi-quantitative fiber dye "fingerprint." 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 discrimination. Such information may also open the possibility of tracing specific dye formulations to the textile manufacturer.

Because dyes adhere to different polymer fibers with different mechanisms, extraction methods must be individually designed to disrupt those mechanisms and provide efficient extraction. For example, for nylon, an extraction solvent mixture of water, pyridine, and ammonia disrupts the electrostatic attraction of acid dyes to nylon; however, a single ultra-performance liquid chromatography method suited for qualitative and semi-quantitative analysis of all three dye types has been developed. Having a single chromatographic method for those three dye classes avoids using multiple chromatographic conditions and increases sample throughput.

Method transfer has been accomplished by the forensic laboratory of the South Carolina Law Enforcement Division (SLED). To maintain American Society of Crime Laboratory Directors/Laboratory Accreditation Board (ASCLD/LAB) accreditation, the Scientific Working Group for Toxicology (SWGTOX) validation guidelines were followed. SWGTOX requires accuracy within 20%, limit of detection and limit of quantitation of 10ng/mL or less, and a percent coefficient of variation less than 20% (within and between run). The method presented here for the three fiber types and each respective dye for Ultra Performance Liquid Chromatography — Diode Array Detection (UPLC-DAD) has resulted in a limit of detection of <570ppb, a limit of quantitation of <1.89ppm, and a coefficient of variation of <3.43% for all tested dyes. Although this approach is destructive to the fiber evidence, the ability to analyze sub-millimeter fiber lengths of single fibers, coupled with detection limits in the hundred picogram range by both DAD and tandem Mass Spectrometry (MS/MS), make routine forensic characterization feasible.

Fiber Analysis, Dye Extraction, UPLC and Mass Spectrometry

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