B140 Forensic Identification of Dyes Extracted From Textile Fibers by Liquid ChromatographyMass Spectrometry (LC-MS)

Min Huang, PhD, and Jehuda Yinon, PhD, National Center for Forensic Science, University of Central Florida, P.O. Box 162367, Orlando, FL*

The goal of this presentation is to present the progress on the development of a method to identify dyes extracted from textile fibers, which will contribute to forensic fiber characterization and comparison.

Textile fiber examination is frequently carried out in forensic laboratories to provide physical evidence in crime investigations. An important part of forensic fiber examination involves the characterization of textile dyestuffs. Currently, there are several methods used for dye analysis, including ultraviolet, visible, and fluorescence microspectrophotometry, infrared spectrometry, and high performance liquid chromatography (HPLC). However, since many hundreds of dyes are used in the textile dying industry, these techniques are not specific enough for their identification, because different dyes may have the same color may have absorption at the same wavelength, or may have very close retention times. Therefore, these methods cannot provide unambiguous forensic identification or comparison. Furthermore, these techniques do not provide chemical structural information, which, in some cases, is crucial to determine the single source of a dye. Being a highly sensitive and selective method, liquid chromatography-mass spectrometry (LC-MS) has the potential to characterize and compare extracted fiber dyes according to their molecular structure. In this study, a LC-MS based method was developed to identify dyes extracted from textile fibers and create a reference database to serve the forensic and law enforcement communities.

An Agilent 1100 MSD quadrupole mass spectrometer equipped with an electrospray ionization (ESI) source and an Agilent 1100 HPLC are used for this study. The instrument can be switched conveniently between a positive ion mode and a negative ion mode, according to a dye's tendency to form negative or positive ions. The dye is extracted into an organic solvent phase from a fiber in a closed system. Heating is necessary in many cases. 5 µL of the extracted sample solution is injected into the LC-MS system. Separation is carried out with a ZORBAX Eclipse XDB-C18 (2.1 x 150 mm) HPLC column. The flow rate of the mobile phase is 0.15 ml/min. Solvent gradient is used to achieve better separation. Parameters for the mass spectrometer are optimized to get the best sensitivity. Drying gas for the ESI is 12.0 L/min. Spray chamber temperature is 350ºC.

Mass spectra were obtained for standard dyes, including disperse dyes, direct dyes, acid dyes, and basic dyes of various typical colors. The detection limit is in the range of several ppb to 100 ppb, depending on the dye's chemical structure. For a 5 µL sample injection this corresponds to an absolute detection limit of 5-500 pg. Type of organic solvent, extraction time, and other factors for the extraction process will be optimized to extract the dyes most efficiently and reduce the amount of fiber necessary for identification.

The most frequent ions in the mass spectra of the analyzed dye standards are $(M-H)^-$, $(M-xNa)^x$(x=1 - 4), $(M+H)^+$, and $(M+Na)^+$, where M represents its molecular form. In the Agilent MSD 1100 it is possible to increase ion fragmentation by increasing a certain voltage in the ion source called "fragmentor voltage." Therefore, information about a dye's chemical structure may be obtained according to its mass spectral fragmentation pattern. This method provides high reliability for dye identification, based on the fragment and molecular ions. A certain number of textile fibers were extracted and then identified by the LC-MS method. Mass spectra of standard dyes and dyes extracted from fibers will be presented and discussed. An Internet reference database of LC-MS mass spectra of dyes will be created for the benefit of the forensic community.

Dyes, Fibers, LC-MS

 ** Presenting Author*