Novel Method for the Forensic Dye Analysis by Direct Analysis in Real Time Mass Spectrometry

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Abstract

The thermal desorption/pyrolysis-direct analysis in real time-mass spectrometry (TD/Py-DART-MS) method was developed for the analysis of an array of blue dyes. Past experiment has shown that the TD/Py-DART-MS can identify the polymeric backbone structures of common textile materials. There are thousands of textile dyes, and these are classified into different categories according to their applications and chemical compositions. The ability to identify an unknown fiber is of great forensic importance, and this evidence can be used to link a suspect's carpet or clothing to a crime scene. This study was comprised of 5 blue dyes from commonly used categories. A TD/Py-DART-MS method was developed to analyze the dyes, which were applied on fibers such as silk, cotton, and nylon. The mass spectra were collected, and the multidimensional profile, including both the physical properties and chemical information, was analyzed and compared in order to obtain the characteristic signals. These were distinguishable from their fiber and other dyes, confirming the sensitivity and discriminatory power of the TD/Py-DART-MS for dyes with the same color. The samples were comparatively analyzed by a Raman microscope method. This method collected both spectroscopic data to be compared to a spectral database, as well as the image of the fiber. This study found that the TD/Py-DART-MS method requires a single fiber sample size and a sample preparation time of approximately 2 minutes, but it offers a profile within approximately 7 minutes. Due to the method being both simple to perform and has high sample throughput potential, this may significantly contribute to the identification of unknown dyes on fibers in comparison to the traditional, slower, and more restrictive methods.

Introduction

Fibers are associative evidence which can be used to establish a link between a suspect and a crime scene. Based on Locard's exchange principle, transfer of material will occur with objects are in contact with each other. Additionally, identification of dyes and pigments on fibers is significant for forensic comparisons because the great variation in production methods makes them highly discriminating characteristics[1]. Microscopy remains a viable option for analysis, especially as reference method, because it is non-destructive[1,2]. However, additional analysis is required, and ideally, to provide the most discriminating information, multiple orthogonal techniques should be used (i.e., inorganic/organic analysis, spectroscopy/chromatography/mass spectrometry methods)[3]. Some examples of these methods are liquid chromatography-mass spectrometry (LC-MS) and thin layer chromatography (TLC)[2,4]. However, solvent extraction of dyes prior to the LC-MS analysis is prone to contamination, and time-consuming (e.g., about 1 hour), and TLC has issues in poor reproducibility along with an inadequate chromatographic resolution of similar dyes[2,4]. As an alternative, direct analysis in real time ionization source coupled with mass spectrometry (DART-MS) can be used not simply as a faster method but as its own stand-alone method to provide a multidimensional chemical profile including mass spectra of similar colored dyes and the polymeric material, along with their respective desorption temperatures, which can be used to differentiate both types of dyes and types of fibers[5].

Materials and Methods

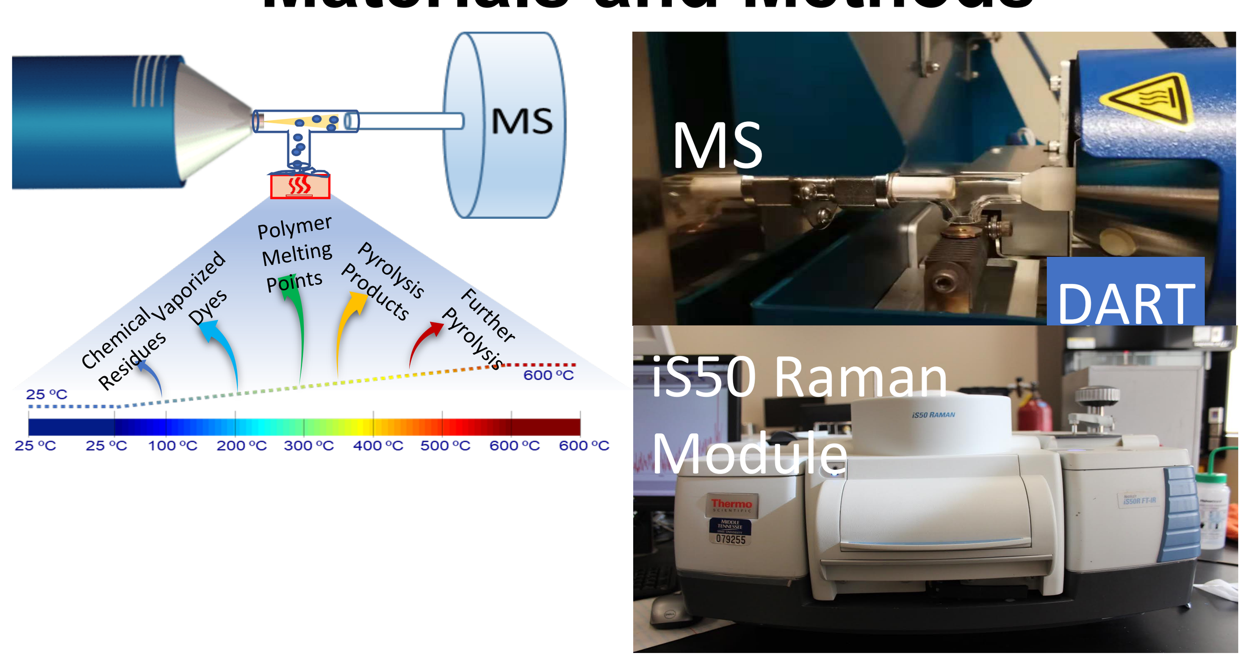

Figure 1. TD/Py-DART-MS. Left: Schematic diagram of TD-DART-MS ; Right: Thermal desorption (TD) module.

- A DART ion source (IonSense, Inc., Saugus, MA) was coupled to a Thermo LTQ XL mass spectrometer (Thermo Scientific, San Jose, CA). The IonRocket system (BioChromato, Inc., San Diego, CA, USA) was used for TD/Py-DART-MS analysis. A Thermo iS50 Raman module (Thermo Scientific, San Jose, CA) was used to collect Raman spectral data.
- For all the DART-MS experiments, the gas stream was maintained at 400 °C with helium as the ionization gas. The mass spectra were collected in a *m/z* range of 50-1000 in positive or negative mode, depending on the dye category
- The dye standards were diluted to a final concentration of 0.1 mg/mL with methanol, and 5.0 µL was transferred to the reservoir of a copper sample pot, dried for 5 min at room temperature, and analyzed by TD/Py-DART-MS.
- The fibers unwound from WarpStrip 8 Fiber Fabric (Testfabrics, Inc.) were dyed using an in-house tie-dye method and deposited with tweezers onto the reservoir of a copper sample pot with 5.0 µL of methanol before the TD/Py-DART-MS analysis.

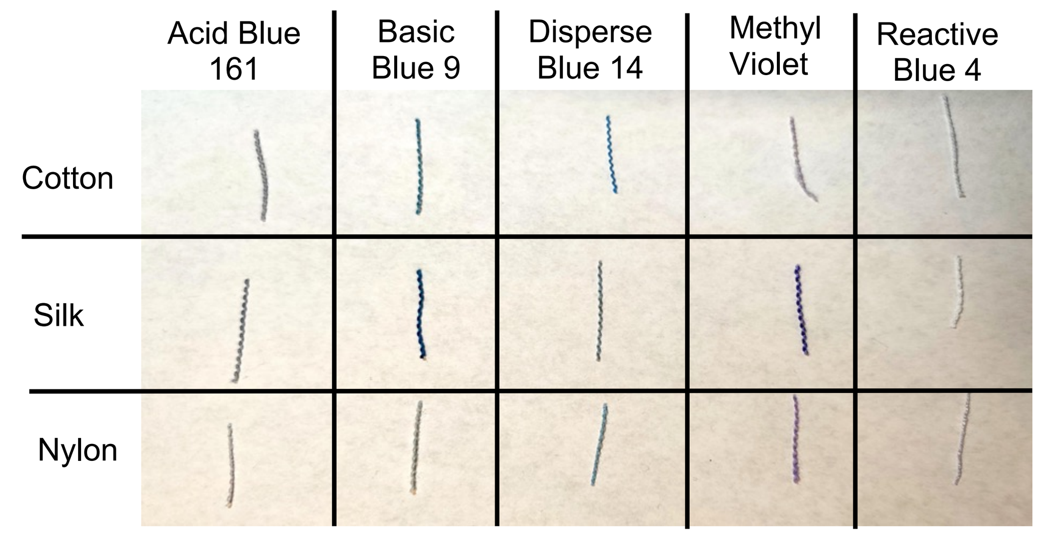

Figure 2. Comparison of 5 dyes applied to 3 common fiber types. Analytical techniques are necessary to discriminate each dyes fiber from others of similar color.

Results

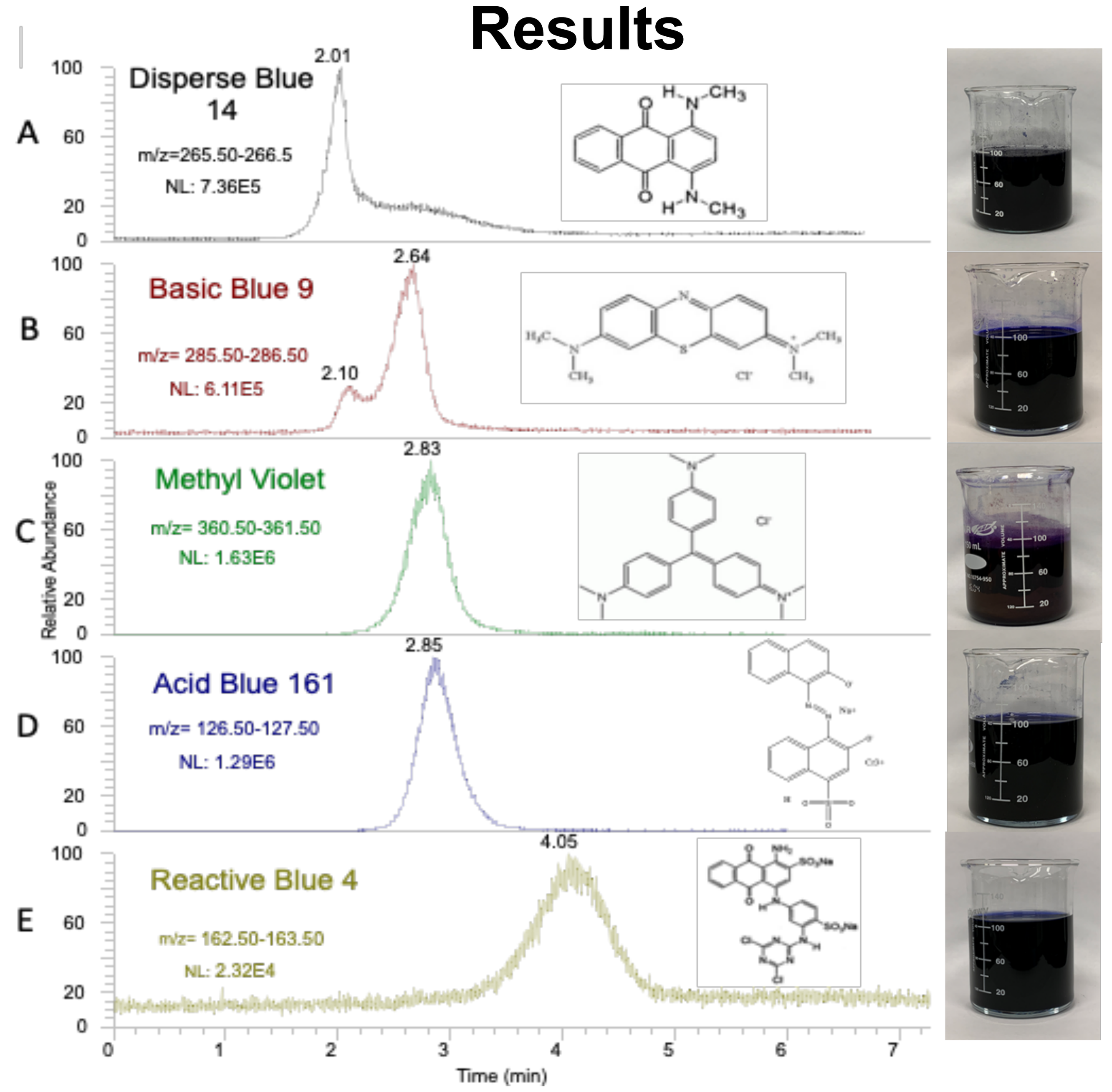

Figure 3: TD/Py DART-MS extracted ion chromatograms of dye standards: Disperse Blue 14 (A), Basic Blue 9 (B), Methyl Violet (C), Acid Blue 161 (D), and Reactive Blue 4 (E). Note: additional molecular structure and image of dye standard solutions are included

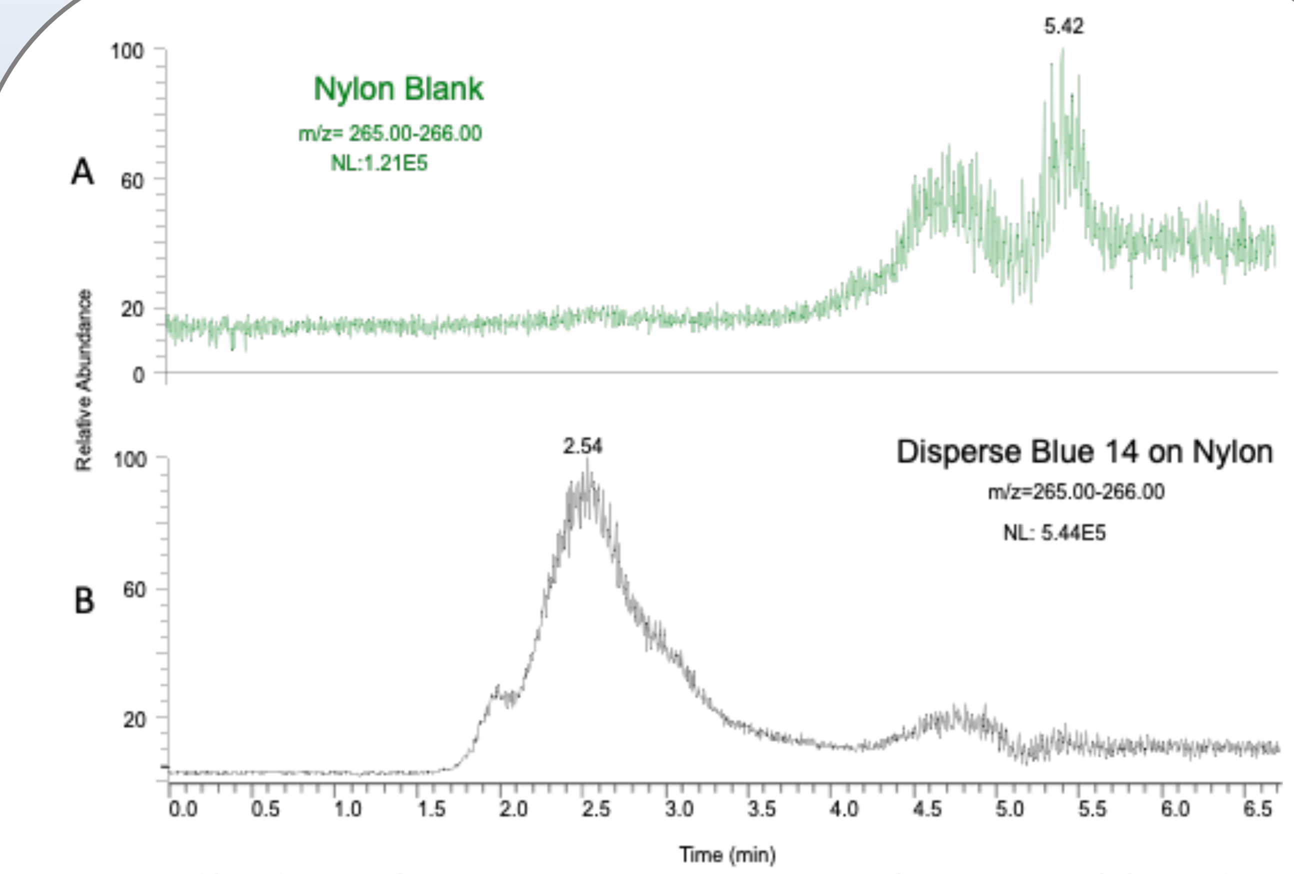

Figure 4: TD/Py DART-MS extracted ion chromatograms of nylon blank (A) and Disperse Blue 14 on nylon fiber (B).

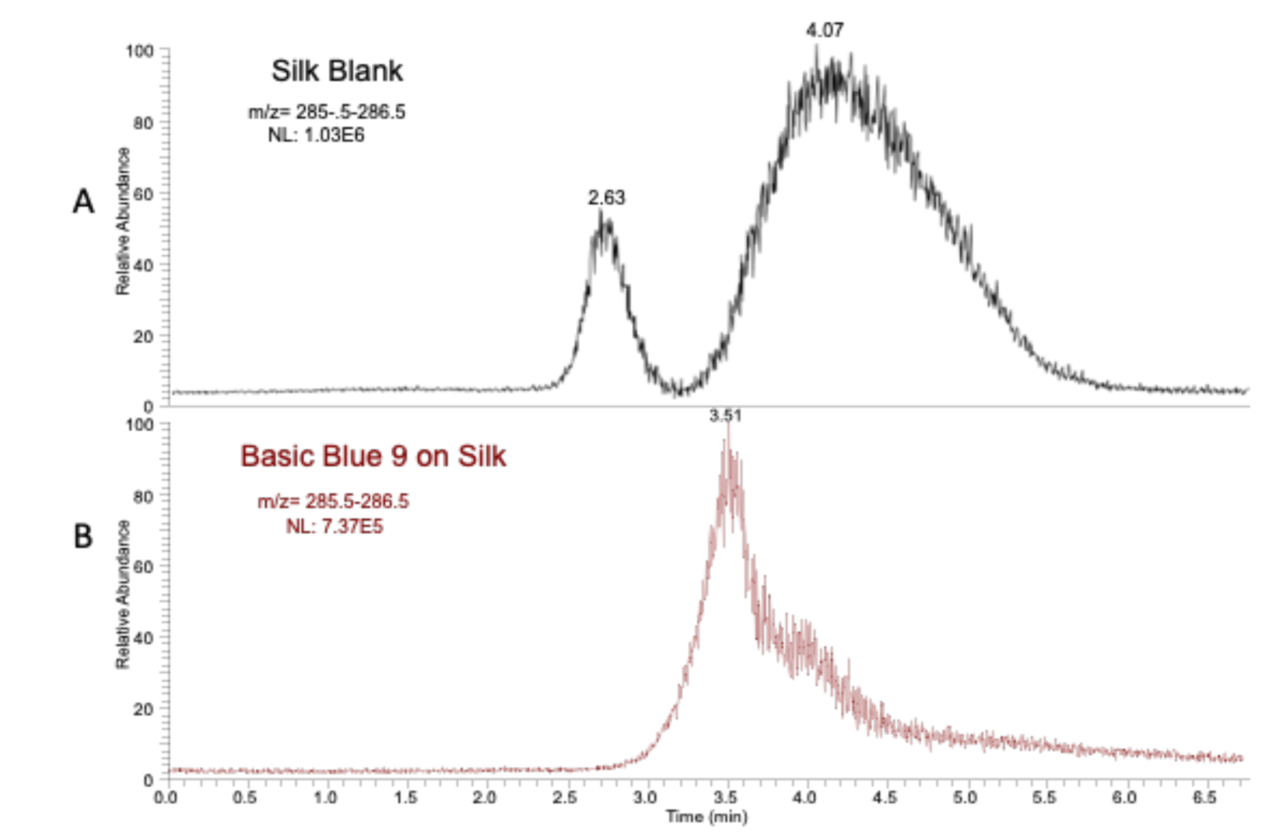

Figure 5: TD/Py DART-MS extracted ion chromatograms of silk blank (A) and Basic Blue 9 on silk fiber (B). Note: Desorption temperatures are similar, but Basic Blue 9 present on silk (B) creates a single distinct peak, rather than 2 peaks present in the silk blank (A).

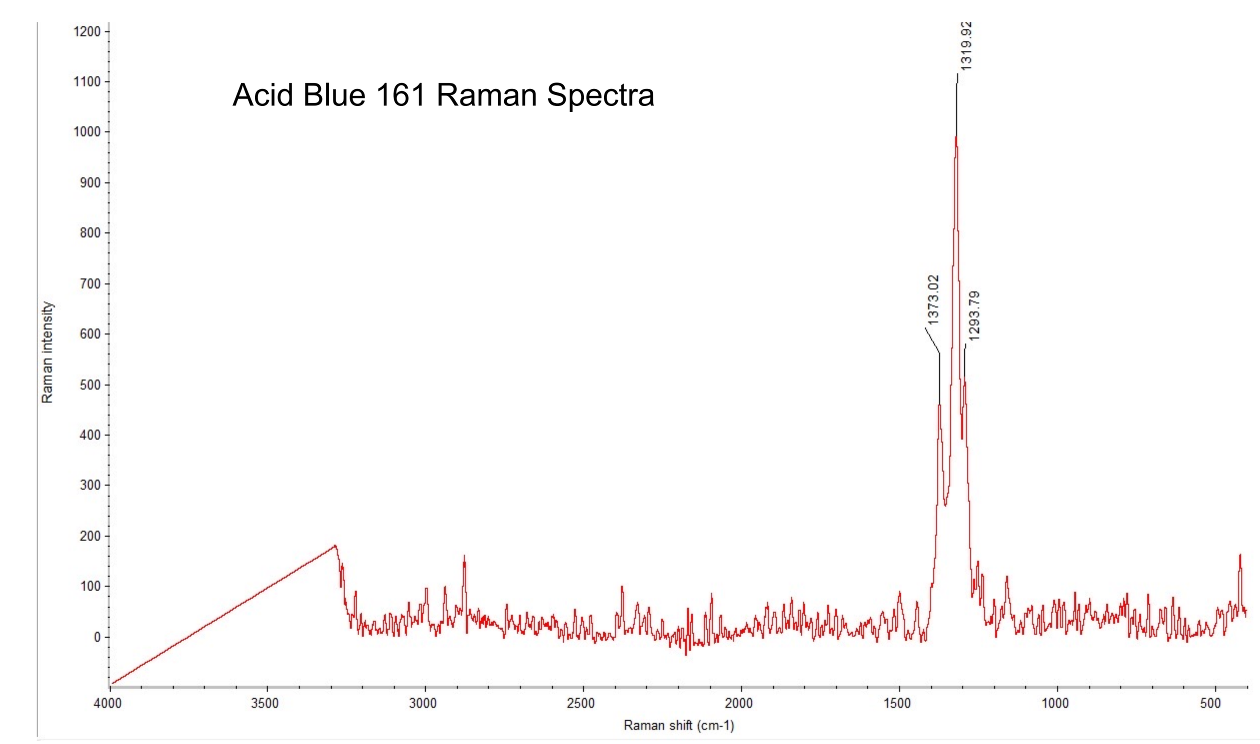

Figure 6: The baseline-corrected Raman spectrum of Acid Blue 161 dye powder collected using a Thermo iS50 FT-Raman spectrometer with 1064 nm laser excitation of the sample. Note: The Raman shift of the peaks are labeled.

Conclusions

- Characteristic ions of dyes on fiber were identified using TD/Py-DART-MS;
- Protonated molecular ions of the standards belonging to Disperse Blue 14, Basic Blue 9, and Methyl Violet were detected; characteristic fragment ions for Acid Blue 161 and Reactive Blue 4 were identified;
- Desorption time/ temperature can aid in the identification of dyes on fiber and the discrimination of individual dyed fibers;
- When the dyes were applied to textile fibers, the desorption time/ temperature for the dye's characteristic ions were shifted higher. This indicated there are possible interactions between the dye and fiber that have tobe taken into account when analyzing unknown fibers.
- The sensitivity of this method varied depending on the type of dyes and fibers; for instance, Methyl Violet produces a higher ion yield compared to Reactive Blue 4;
- Thermo iS50 Raman module could be used to acquire distinctive spectra for each dye category and to identify specific dyes via spectral search of commercial or custom spectral databases.

Future Study

- More types of dyes on different fabric materials will be analyzed with TD/Py DART-MS and Raman spectroscopy;
- Characteristic signals from dyes with larger molecular weights, such as Acid Blue 161, will be investigated to pinpoint specific breakages in the molecule, and other stable fragments;
- More dyes within each category will be analyzed to further evaluate the discriminatory power of DART-MS;
- Raman microscopy technique will be applied to more dyes in this study, and the results will be compared with TD/Py DART-MS results;

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Acknowledgments

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