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

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Abstract

The thermal desorption/re留下了direct analysis in real-time mass spectrometry (TD-DART-MS) method was developed for the analysis of an array of blue dyes. Past experiments have shown that the TD-DART-MS method can identify the polymeric backbone structures of common forensic fibers. However, thousands of textile dyes, and these are classified into different categories according to their applications and performances in the forensic and chemical compositions. The characteristic ions can be used in the identification of forensic fibers. This study was developed to analyze forensic fibers. The TD-DART-MS method was developed to analyze the fibers, which were applied on fabrics such as silk, cotton, and nylon. The mass spectra were collected, and the multidimensional analysis, including both the physical properties and chemical analysis, was compared and utilized in the identification of forensic fibers. This study was conducted to identify the unknown dyes on fibers in comparison to the traditional, slower, and more expensive methods.

Introduction

Analytical techniques for the identification of dyes and pigments on fibers are significant for forensic comparisons because the great variation in production methods makes them highly discriminating characteristics. Microscopy remains a viable option for analysis, especially as reference methods, because it is non-destructive. However, additional analysis is required, and ideally, to provide the most discriminating information, multiple orthogonal techniques should be used (i.e., macroscopic/ microscopic analysis, spectroscopy/microscopy/mass spectrometry). Some examples of these methods are liquid chromatography-mass spectrometry (LC-MS) and thin-layer chromatography (TLC). However, solvent extraction of dyes prior to the LC-MS analysis, and the extraction of dyes prior to contamination, and the analysis (e.g., about 1 hour), and TLC has issues in poor reproducibility along with an inadequate chromatographic resolution of dyes. As an alternative, direct analysis in real-time ionization source coupled with mass spectrometry (DART-MS) can be used not simply as a stand-alone method to identify a multi-dimensional chemical profile including mass spectra of similar colored dyes and the polymeric backbone structures with their respective desorption temperatures, which can be used to differentiate both types of dyes and types of fibers.

Materials and Methods

A DART ion source (IontoScience, Inc., Saxaux, MA) was coupled to a Thermo LTQ XL mass spectrometer (Thermo Scientific, San Jose, CA). The IontoPocket system (BioCromatec, Inc., San Diego, CA, USA) was used for TD-DART-MS analysis. A Thermo 9500 Raman module (Thermo Scientific, San Jose, CA) was used to analyze the fibers. For all the TD-DART-MS experiments, the gas stream was maintained at 400 °C with nitrogen as carrier gas. The mass spectra were collected in a m/z range of 50-1000 in positive polar mode, depending on the dye category. The dyes standards were dissolved in a final concentration of 1 mg/ml with methanol, and 3.5 μl was transferred to the reservoir of a copper sample pot, dried for 5 min at room temperature, and analyzed by TD-PDFT-DART-MS. The fibers were cut from WarpStrip silk fabric (Tetrafabrics, Inc.) and were dyed using an in-house dyeing method and decomposed with hexane once the solution was confirmed to be non-volatile. The fibers were analyzed with Thermo LTQ FT-MS spectrometer.

Dye analysis can be achieved by direct analysis in real time mass spectrometry (TD-DART-MS). Time-resolved mass spectrometry was used to analyze forensic fibers. A new method was developed to analyze the fibers, which were applied on fabrics such as silk, cotton, and nylon. The mass spectra were collected, and the multidimensional analysis, including both the physical properties and chemical analysis, was compared and utilized in the identification of forensic fibers. This study was conducted to identify the unknown dyes on fibers in comparison to the traditional, slower, and more expensive methods.

Results

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

Figure 3. TD-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-PDFT-DART-MS extracted ion chromatograms of nylon black (A) and Disperse Blue 14 on nylon fiber (B).

Figure 5. TD-DART-MS extracted ion chromatograms of silk black (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 peaks present in the silk blank (A).

Figure 6. The baseline-corrected Raman spectrum of Acid Blue 161 dye powder collected using a Thermo 950 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-DART-MS.
• Protomolecule 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 temperatures were useful 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 taken into account when analyzing the characteristics.
• The sensitivity of this method varied depending on the type of dyes and fibers, for example, a copper sample pot with 5.0 μl of methanol before the TD-DART-MS analysis.

Future Study

• More types of dyes on different fabric materials will be analyzed with TD-DPART-MS and Raman spectrometry.
• Characteristic signals from dyes with larger molecular weights, such as Acid Blue 161, will be investigated to pinpoint specific breakdowns 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-PDFT-MS results.

References


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