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

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Introduction

A forensic examiner should perform a combination of methods to characterize fiber evidence, along with providing a complete and specific description of an item, rigorously assessing its uniqueness, and value as evidence. Today, the identification or the comparison of fibers requires an examiner to perform at least two analytical techniques for each of the following categories: generic class, physical characteristics, and color (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). The identification of dyes and pigments on fibers is significant for forensic comparisons because the great variation in production methods makes them highly discriminating characteristics. Mass spectrometry has become an increasingly in-demand technique for dye analysis, especially when a fiber is aged or lightly colored (6, 10). A mass spectrometer measures the weight of the molecules in the term of mass-to-charge ratios, which can be used to elucidate the structural identify of chemical compounds (1). Liquid chromatography-mass spectrometry (LC-MS) is a classical methods for dye analysis (3, 4). However, solvent extraction of dyes prior to the LC-MS analysis is critical to the success of dye analysis, but it is laborious, prone to contamination, and time-consuming (e.g., about 1 hour).

As an alternative, this study proposes to use the direct analysis in real time ionization source coupled with mass spectrometry (DART-MS) not simply as a faster method but as its own stand-alone method to provide a multidimensional chemical profile of fiber evidence such as the mass spectra of both the dye and polymeric material and their respective desorption temperatures, which can be used to differentiate fibers. DART-MS instruments are also becoming increasingly available in the crime labs for drug and paint analysis (5, 6-7), and its applications in forensic science continues to grow. DART-MS has already demonstrated the potential of fast fiber analysis with minimal sample preparation (3, 8) , however the existing methods require large amount of textile fibers and easily contaminate mass spectrometers after multiple analysis which are not suitable for high-throughput forensic fiber analysis. A thermal desorption/pyrolysis device coupled with DART-MS (named TD-DART-MS) is proposed in this study to characterize various fibers. A programmable temperature gradient (up to 600 °C) can be applied in TD-DART-MS method (Figure 1), allowing compounds on the single fiber to be pyrolyzed and/or vaporized along the temperature gradient before mass spectrometric analysis. Although TD-DART-MS does not need extra sample extraction and chromatographic separation, it partially preserves advantages of extraction and separation.

Materials and Methods

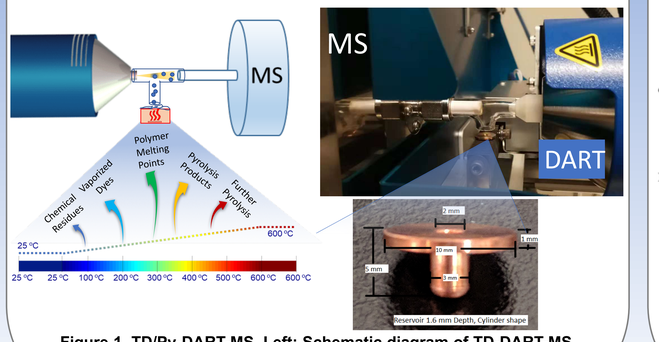

Figure 1. TD/Py-DART-MS. Left: Schematic diagram of TD-DART-MS ; Right: Thermal desorption (TD) module.

- 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;
- For all the DART-MS experiments, the gas stream was maintained at 500 °C with helium as the ionization gas. The mass spectra were collected in a *m/z* range of 50-600 in positive mode;
- A total of 9 blue dyes from four categories, acid, basic, reactive, and vat, and methyl violet were aligned for analysis. Dye standards were purchased from TCI America Co., LTD.
- Warp Stripe 8 Fiber Fabric strips (Testfabrics, Inc.) will be the primary fabric used. This rectangular sheet of fabric includes segments of Filament Acetate, Bleached Cotton, Nylon 6.6, Spun Polyester, and others to imitate the common fabrics the dyes would be processed with.
- Fabric was washed in Na_2CO_3 and warm water and were dyed in a 1:1 dye powder, methanol solution using the "tie-dye" technique. Excess dye was washed out after 24 hours.
- The fibers unwound from dry threads were cut into 5−15 mm lengths (about 30−100 µg) 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. The dye standards were diluted to a final concentration of 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.

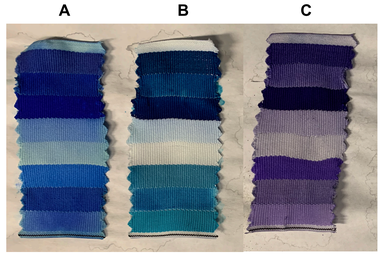

Figure 2. Warp Stripe 8 Fabric Strips dyed with Basic Blue 7 (A), Basic Blue 9 (B), and Methyl Violet (C)

Aims

- To distinguish and differentiate textile dyes based on their mass spectra.
- Minimize the amount of fiber ran and minimize preparation time.
- To distinguish textile dyes from the fibers based on both physical and chemical properties.
- Recreate a natural environment by testing dyes with their commonly associated fabrics.
- Determine an ideal solvent for variety of dyes.
- Validate findings by Raman microscopy, a well-known, non-destructive instrument for trace fiber analysis.

Results

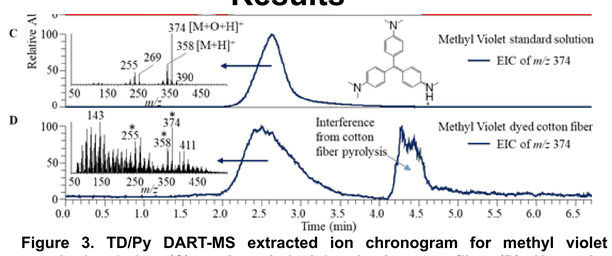

Figure 3. TD/Py DART-MS extracted ion chronogram for methyl violet standard solution (C), and methyl violet dyed cotton fiber (D). Note: the characteristic ions for dyes were labeled by asterisk (*) in the mass spectra.

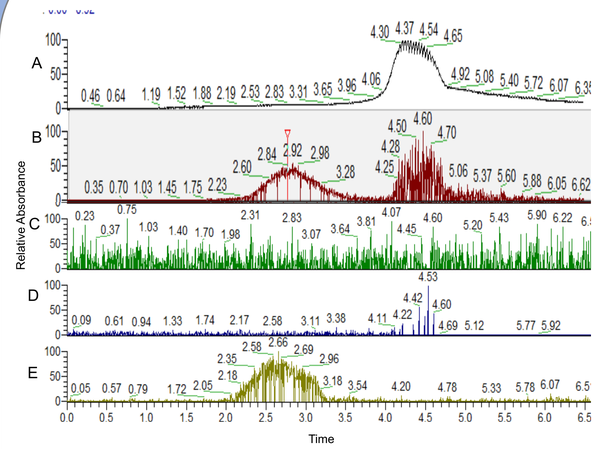

Figure 4. TD/Py DART-MS mass spectra comparison of cotton fiber blank (A), Basic Blue 7 on cotton (B), methanol blank (C), Na_2CO_3 blank (D), and Basic Blue 7 blank (E).

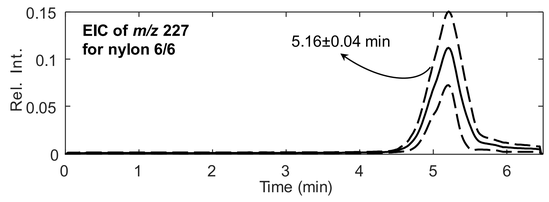

Figure 5. The average EIC of characteristic ions for nylon 6/6 fibers (n = 9). Previous studies confirmed, with 97% certainty on the location and signal of fibers used in this study.

Future Directions

- Under unforeseen circumstances, 6 of the 9 dyes were not able to be tested. These will be ran to strengthen the results and conclusions of this experiment.
- These samples will be ran in a standard Raman microscope, in the fall of 2020, for validation of the TD/DART-MS by a commonly used instrument in forensic microanalysis labs.
- The conclusions of a limiting molecular weight should be expanded upon further to investigate the instruments limitations.
- Samples of clothing, dyed blue, should be added to this analysis as unknown samples for the known results to be compared to.

Conclusions

- Characteristic ions of fibers and dyes were identified using TD/Py-DART-MS, both on separate mass spectra, and when they were ran together;
- TD/Py DART-MS shows promising potential for the high-throughput analysis of fibers and dyes with great discriminating power;
- The TD DART-MS was able to analyze dyes on fibers which appears light and had a minimal amount of material in comparison to classic methods. This contributes to sensitivities of the TD/DART-MS and the usefulness of those sensitives in trace analysis;
- Each positive analysis yielded signals within the unique mass range of a dyes' molecular mass, indicating that the structure of the dye was responsible, and no others, see Figure 3;
- Preliminary tests using the dyes, Disperse Blue 1-2 and Acid Blue 45 yielded no results due to their incredibly large molecular weight. The dyes ran in this study were all of a molecular weight of less than 800 g/mol, and, through the comparison of the signals with no other changes, it can be concluded that the TD/DART-MS has a limit to its indication. This is most likely due to these larger molecules being less volatile. This can be a useful aspect when applying the TD/DART-MS to unknown fibers.
- The lack of full signals of the before mentioned large dyes were traced to SO_3 groups, leading the conclusion to be that the temperature gradient causes fractures in large dyes.
- The physical discrepancies between the melting points each fiber used was observed with a naked eye comparison. This information can offer easily extractable information in comparing an unknown sample to known samples.
- The temperature gradient used in past analysis of textile fibers was concluded to be ideal, with a total analysis time of approximately 7 minutes. This confirmation came after a test of QuickStrip analysis, in which no dye signals appears. However, a gradient up to 600ºC detected both dyes and fibers.

References

1. Schotman, Tom, G., Application of dye analysis in forensic fibre and textile examination: Case Examples, *Forensic Science International,* 278, 2017, 338-350
2. Mistek, Ewlina, et al., Toward Locard's Exchange Principle: Recent Developments in Forensic Trace Evidence Analysis, *Analytical Chemistry,* 91, 2019, 637-654
3. Armiage, Ruth A., et al., "Direct Analysis in real time-mass spectroscopy for identification of red dye colorants in Paracas Necropolis Textiles" *Science and Technology of Archeaological Research (STAR),* 1 (2), July 2015, pg. 62-68
4. Sultana, Nadia, et al., Direct Analysis of textile dyes from trace fibers by automated microfluidic extraction system coupled with Q-TOF mass spectrometer for forensic application, *Forensic Science International,* 2018, 67-73
5. Robinson, Elizabeth L., Sisco, Edward, Detection of Brodifacoum and other Rodenticides in Drug Mixtures using Thermal Desorption Direct Analysis in Real Time Mass Spectrometry (TD-DART-MS), *Journal of Forensic Science,* 64 (4), 2019, 1026-1033
6. Sisco, Edward, et al., What's in the bag? Analysis of exterior drug packaging by TD-DART-MS to predict the contents, *Forensic Science International,* 304, 2019, 1-7
7. Maric, Mark et al., DART-MS: A New Analytical Technique for Forensic Paint Analysis, *Analytical Chemistry,* 90 (11), 2018, 6877-6883
8. Deroo, Cathy S., Armitage, Ruth A., Direct Identification of Dyes in Textiles by Direct Analysis in Real Time-Time of Flight Mass Spectrometry, *Analytical Chemistry,* 2011, 6924-6928

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