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Direct Analysis of Textile Fabrics and Dyes Using IR Matrix-Assisted Laser Desorption Electrospray Ionization (MALDESI) Mass Spectrometry

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Abstract

The forensic analysis of textile fibers uses a variety of techniques from microscopy to spectroscopy. One such technique that is often used to identify the dye(s) within the fiber is mass spectrometry (MS). In the traditional MS method, the dye must be extracted from the fabric and the dye components are separated by chromatography prior to mass spectrometric analysis. Direct analysis of the dye from the fabric allows the omission of the lengthy sample preparation involved in extraction, thereby significantly reducing the overall analysis time. Herein, a direct analysis of dyed textile fabric was performed using the infrared matrix-assisted laser desorption electrospray ionization (IR-MALDESI) source for MS. In MALDESI, an IR laser with wavelength tuned to 2.94 μm is used to desorb the dye from the fabric sample with the aid of water as the matrix. The desorbed dye molecules are then post-ionized by electrospray ionization (ESI). A variety of dye classes were analyzed from various fabrics with little to no sample preparation allowing for the identification of the dye mass and in some cases the fiber polymer. Those dyes that were not detected using MALDESI were also not observed by direct infusion ESI of the dye standard.

INTRODUCTION

Textile fibers are a significant form of trace evidence in forensic investigation. The importance of trace evidence is based primarily on Locard's exchange principle which states that a transfer of evidence occurs when a person comes into contact with any object or another person. This axiom allows for a comparison of fibers to determine the probability of association, *i.e.* fibers from the victim compared to fibers from the suspect, or fibers from the suspect matched against the crime scene, etc. If unrelated fibers positively match, the probability of deliberate contact increases while the probability of coincidental contact decreases.¹ The importance of unrelated fibers being compared with confidence will ensure viability of evidence in court necessitates that the techniques used for analysis be as accurate, time efficient, widely available, and up-to-date as possible. The analytical techniques used for contemporary fiber analysis include both non-destructive and destructive methods. Non-destructive methods yield the fiber polymer, information about

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SUPPORTING INFORMATION Tables for providing the chemical structure, exact mass, and observed mass can be found in the supporting information. A series of figures which show the MALDESI mass spectra for each of the observed dyes is also available in the supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

the polymer such as refractive indices, luster, and birefringence, and the basic dye color. However, non-destructive methods will not provide the significantly more conclusive data such as the dye's mass and elemental composition.²

Non-destructive techniques include microscopy, spectroscopy, and ultraviolet-visible microspectrophotometry (UV-vis MSP). The forms of microscopy commonly used for forensic purposes are confocal microscopy,³ Fourier transform infrared (FT-IR) microscopy,⁴ polarized light microscopy,¹ comparison microscopy,^{2, 5} and scanning electron microscopy with energy dispersive spectrometry (SEM-EDS).¹ Microscopy is used primarily to determine and compare fiber polymers of unrelated fibers, examine fraying and cuts, and identify polymer characteristics such as striations, crimp, and cross-sectional shapes.² The spectroscopic techniques used in forensics are Raman spectroscopy,⁶⁻⁷ FT-IR spectroscopy,⁴ and X-ray fluorescence spectroscopy.⁷ Spectroscopy is used to definitively determine the fiber polymer and polymer composition, and some forms of spectroscopy such as Raman will yield limited qualitative dye information such as basic color spectra and dye concentrations. Spectroscopy will not give the quantitative dye mass or elemental composition.^{1, 6-7} UV-vis MSP is a combination of both microscopy and spectroscopy. Its forensic use is specifically for comparison purposes because UV-vis MSP can identify spectral characteristics but cannot differentiate dyes and dye mixtures.¹ These techniques have the benefits of being non-destructive while requiring little to no sample preparation. These benefits are crucial to forensic labs, which usually have very small sample sizes, limited analysts, and are on strict time constraints.

Liquid chromatography mass spectrometry (LC-MS) is becoming an increasingly popular method for identifying dye(s) from dyed textile fiber with a high degree of molecular specificity. LC-MS has the benefit of yielding the mass of the dye and in some instances the fiber polymer. A few of the disadvantages, however, include the destructive nature of the analysis as well as the extensive sample preparation procedures which can lead to lengthy analysis times. Prior to LC-MS analysis the dye must first be extracted from the fiber using an extraction solvent specific to the dye class. The extracted dye(s) can then be loaded onto an LC column for separation and subsequent detection by mass spectrometry. The entire extraction/chromatography/mass spectrometry process is lengthy, resulting in analysis times of around an hour, and extraction of the dye from the fiber renders the fiber unusable for any other subsequent characterization.^{1, 8-12}

Direct analysis of textile fibers can provide information about the dye, similar to that which can be obtained from LC-MS, in a much shorter period of time while requiring little to no sample preparation. Direct analysis techniques such as laser desorption photoionization^{13,14} and direct analysis in real time¹⁵ (DART) have been used to identify the dyes present in textiles. Herein, matrix-assisted laser desorption electrospray ionization (MALDESI)¹⁶ coupled to MS is used for the direct analysis of dyes from textile fibers.

In IR-MALDESI, a mid-IR laser tuned to 2.94 μm is pulsed into a water containing sample to desorb neutral molecules which partition into an orthogonal electrospray plume where they are ionized by an ESI-like process.^{17,18} The laser wavelength correlates with the absorption maximum for the symmetric and asymmetric OH stretching modes in water. Using water as a matrix is ideal because it does not interfere with the mass spectrum and produces a low background signal. The low background signal enables better detection of the ions of interest. For the direct analysis of textile fabric that is presented herein, water is added onto the fabric sample to absorb the laser energy and facilitate the desorption of the dye molecules for subsequent post-ionization by ESI. The MALDESI source is coupled to a high mass accuracy-high resolving power hybrid linear ion trap, Fourier transform ion cyclotron resonance (LTQ-FT-ICR) mass spectrometer. The FT-ICR mass spectrometer's

high resolving power and high mass accuracy allows the determination of elemental composition of the dyes. It should be noted that new bench-top generations of hybrid FTMS instruments can provide equivalent information. If the molecules are fragmented using tandem mass spectrometry (MS/MS), structural information about the compound can be determined as well. Structural information is very important when identifying dyes in forensics because many of the dyes have similar structures. Some dye structures differ by only a single substituent.¹⁹

The direct analysis using MALDESI is beneficial in that there is no extraction required, meaning the fiber can be used for multiple analyses because such an insignificant amount of fiber is consumed. MALDESI is time efficient, taking a few seconds to analyze the fiber and dye, while traditional LC-MS methods take around an hour for total analysis. The only sample preparation necessary for MALDESI is spotting a few droplets of water on the fabric to absorb the laser energy and facilitate the desorption of the dye.

EXPERIMENTAL

Materials

Dyes were obtained from the stored supplies at the NCSU College of Textiles. Acid black 58, blue 40, and green 16 were purchased from Ciba-Geigy (Dover Township, NJ, USA). Basic Violet 16 was purchased from Clariant (Charlotte, NC, USA). Disperse red 60 and blue 79 were purchased from M. Dohmen (Greenville, NC, USA). Indigo, pigment red 146 and red 112 were purchased Huntsman (Charlotte, NC, USA). Direct red 24 was purchased from Crompton and Knowles (Middlebury, CT, USA). Vat orange 7 was purchased from Dystar (Charlotte, NC, USA). The reactive dyes (red 141, blue 160, and yellow 84) were purchased from the Institute of Dyes and Organic Products (Zgierz, Poland). HPLC grade acetonitrile and water were purchased from Burdick and Jackson (Muskegon, MI, USA). The raw fabrics were also obtained from the NCSU College of Textiles supplies.

Direct Infusion ESI

Dyes from a variety of dye classes (acid, basic, disperse, pigment, vat, and reactive dyes) were chosen for direct analysis from different fabrics (nylon, acetate, polyester, and cotton). A small database of mass spectra was developed by directly infusing standard solutions made from the raw dye powders. Dye standards were made by dissolving 1 mg of the raw dye powder in 1 mL of 50:50 (v : v) water : acetonitrile then diluting the solution to 1 μ M with the electrospray solvent (50 : 50 water : acetonitrile with 0.1% acetic acid). The dye standard solutions were then analyzed by direct infusion ESI in both positive and negative ion modes.

Direct Analysis by MALDESI

The raw un-dyed fabrics were directly analyzed by MALDESI in both positive and negative ion modes to generate representative spectra for each fabric. The raw fabrics were then dyed using the appropriate procedures for the dye class and fabric type (actual procedures can be found in the supplementary material). A 1 cm by 1 cm square was cut from each of the dyed fabrics and these samples were analyzed by MALDESI in both positive and negative ion mode to identify the dye and, in some cases, the fiber polymer. Each fabric was analyzed as a pixel array of 5 pixels per line and 4 lines. Three laser pulses were fired per pixel with a single mass spectrum acquired after the third pulse and the spacing between pixels and lines was set to 0.5 mm. This correlates to a sampled section that was 2.5 mm by 2 mm for each fabric. While such a large section of the fabric was analyzed, it should be noted that signal from the dye and/or fabric can be obtained from a single pixel which corresponds a sample size that is on the order of the laser spot size that has a diameter of roughly 200 μ m.

Multiple pixels were analyzed across the fabric surface in order to determine the average response. Microscopic images of the dyed fabric surfaces were obtained both before and after MALDESI analysis to provide qualitative information on the level of destruction to the fabric caused by the laser ablation.

IR-MALDESI Source

The IR-MALDESI source parameters were recently optimized using a design of experiments¹⁸ and control over the laser ablation and mass spectrometer scanning features have been implemented. Briefly, electrospray solvent (50 % aqueous acetonitrile with 0.1% acetic acid) is pumped through a 75 μm fused silica emitter which is tapered to 30 μm at the tip (New Objective, Woburn, MA) at a flow rate of 200 nL/min. A potential of around 2 kV was applied to a stainless steel microtight union (Upchurch Scientific, Oak Harbor, WA, USA) just before the emitter to generate a stable electrospray. The emitter was held 9 mm from and on axis with the inlet to the mass spectrometer. The fabric sample was placed on a glass microscope slide and was wet with roughly 20 μL of water. It should be noted that this wetting process could theoretically extract some of the dye from the fabric. The fabric sample (dyed or un-dyed) was then placed on a vertical translation stage mounted on a motion controlled XY stage (LTA-HS, Newport Corporation, Irvine, CA, USA) such that the top of the fiber sample was 5 mm below the electrospray axis. A tunable wavelength mid infrared laser (IR Opolette, Opotek, Carlsbad, CA, USA) was used to ablate the fiber sample. The wavelength was tuned to 2.94 μm , corresponding with the symmetric and asymmetric OH stretching frequency, allowing for the water added to the fabric sample to act as an exogenous matrix by absorbing the laser energy and facilitating the desorption of particulates of fiber. The laser beam was steered by three silver coated mirrors (Newport Corporation, Irvine, CA, USA) and was focused onto the sample by a CaF_2 plano-convex lens (Edmund Optics, Barrington, NJ, USA)

LTQ-FT-ICR Mass Spectrometer

The IR-MALDESI source was coupled to a LTQ-FT-ICR Ultra (Thermo Fisher Scientific, San Jose, Ca, USA). An extended capillary was used to allow the stage clearance while rastering the sample. An extended ion transfer tube was used which protruded 23mm from the instrument. The internal diameter of the ion transfer tube was 0.596 mm to maintain the conductance and pressure in the first pumping stage as compared to the original instrument ion transfer tube. For positive mode analyses, the capillary temperature and voltage were set at 250°C and 37 V respectively with a tube lens voltage of 110 V. For negative mode analysis, these values were set to 250°C, -45 V, and -30 V respectively. The resolving power of the FT-ICR was set to 100 000 FWHM at m/z 400 unless otherwise specified. The automatic gain control (AGC) on the LTQ is a short prescan which roughly determines the number of ions that are currently entering the instrument and adjusts the ion trap injection time accordingly such that a similar number of ions are sent to the ICR cell which each scan.²⁰ This adjustment is used to reduce space charge effects and maintain accurate mass measurements.²¹ For the direct infusion ESI experiments the AGC was set to 5×10^5 . In the MALDESI experiment, ions are generated in distinct packets, milliseconds after each laser pulse, rather than being continuously generated. Considering this, the ions would not be present during the AGC prescan, making it impractical to use. For this reason the AGC was turned off and the ion injection time was set to 150 ms to capture ions from all three laser pulses (3 pulses at 20 Hz takes roughly 100 ms from the first pulse). While turning off the AGC can result in poor mass measurement accuracy, the dye ions detected were within 2 ppm of their theoretical mass which is within the instrument specifications.

Data Analysis

Using high resolving power and high mass accuracy instrumentation, such as the FT-ICR, allows for resolution of elemental contributions to isotopic peaks (such as the contribution of ^{34}S in the A+2 peak of a sulfur containing ion).²² Sulfur counting was carried out by comparing the relative abundance of the sulfur peak to the monoisotopic peak and multiplying by the ratio of the isotopic distributions for ^{32}S and ^{34}S ($^{32}\text{S}:^{34}\text{S}$), Equation 1 (adapted from equation 3 in reference 23). $A_{+2\text{Experimental}}$ is the experimental peak intensity of the ^{34}S peak and $A_{\text{Experimental}}$ is the experimental peak intensity of the monoisotopic peak. $^{32}\text{S}_{\text{Theoretical}}$ and $^{34}\text{S}_{\text{Theoretical}}$ are the natural isotopic distributions of the ^{32}S and ^{34}S isotopes, respectively, as reported by the NIST.²³

$$\frac{A_{+2\text{Experimental}}}{A_{\text{Experimental}}} \times \frac{^{32}\text{S}_{\text{Theoretical}}}{^{34}\text{S}_{\text{Theoretical}}} = \# \text{ of Sulfurs} \quad (\text{Eqn. 1})$$

Carbon counting is carried out the same way except the carbon isotopes ^{12}C and ^{13}C replace ^{32}S and ^{34}S , respectively, and the A+1 carbon peak is used in place of the A+2 sulfur peak, Equation 2.

$$\frac{A_{+1\text{Experimental}}}{A_{\text{Experimental}}} \times \frac{^{12}\text{C}_{\text{Theoretical}}}{^{13}\text{C}_{\text{Theoretical}}} = \# \text{ of Carbons} \quad (\text{Eqn. 2})$$

RESULTS and DISCUSSION

The dyes that successfully yielded spectral results were Acid Black 58 (nylon), Acid Blue 40 (nylon), Acid Green 16 (nylon), Basic Violet 16 (acetate), and Disperse Red 60 (polyester). The only polymer peaks that were observed were nylon 6 peaks from the acid dyed fabrics. 487 and 713 as well as 511 and 737 are 226 mass to charge (m/z) units apart which corresponds to a monomer of nylon 6, detectable in negative ion mode. There were no distinguishing peaks for acetate, polyester, or cotton.

Acid Black 58 was detected in negative ion mode as $[\text{M}]^-$. The observed mass from the MALDESI analysis was within 0.68 ppm of the theoretical monoisotopic mass based on the structure provided by the Colour Index International. The theoretical isotopic distribution was calculated and plotted as red circles over the experimental isotopic distribution from direct infusion ESI (Figure 1a) and the direct analysis by MALDESI (Figure 1b inset). The presence of chromium in the structure gives rise to the characteristic shifts seen in the isotopic distribution. The peak pairs at m/z 487 and 713 as well as 511 and 737 in the full scan MALDESI spectrum correspond to polymers of nylon 6 (green squares in Figure 1b). The mass difference between each pair (226 m/z units) relates to the loss of a monomer of nylon 6. Figure 1c shows the before image of the fabric prior to analysis, the portion of the fabric that was analyzed (white square), as well as an image of the sampled area taken after the analysis. This particular fabric had the appearance of damaged fibers across the entire sample, but the “before MALDESI” microscopic image (Figure 1c) clearly shows frizzy, ravaged fibers even prior to analysis. The “after MALDESI” image (Figure 1c) shows the sampled region in the upper left corner of the fabric that appears to be more damaged.

The MALDESI analysis of Acid Blue 40 in nylon led to the observation that the experimental mass of the dye ion $[\text{M}-\text{H}]^-$ (423.0649) did not match the monoisotopic mass (based on the 450.0765) structure provided by the Colour Index International (Figure S1a). It is unknown whether this is due to degradation or contamination of the dye, however, the dye mass observed in the MALDESI analysis (Figure 2b) correlated with the mass observed

from the direct infusion ESI of the dye standard (Figure 2a). This correlation implies that the mass discrepancy with the Colour Index structure is not due to a fragmentation specifically during the MALDESI analysis. To further investigate this discrepancy, the dye standard was directly infused (negative ion mode) and analyzed by tandem MS with collision-induced dissociation (CID) to elucidate its structure. The fragmentation of the parent ion at 423 led to a major fragment at 408.0430, a neutral loss of 15.0219 m/z , which is most likely a loss of a methyl group (Figure S1c). A methyl loss is not a likely fragment to come from the structure from the Colour Index. At a resolving power of 100 000 the contribution of ^{34}S in the A+2 peak can be resolved allowing for sulfur counting to be performed. Using equation 1, it was determined that the molecule contains a single sulfur and carbon counting, using equation 2, was performed and yielded around 21 carbons. With the accurate mass of the parent ion and the information obtained from the MS/MS data, sulfur counting, and carbon counting, a new structure was proposed (Figure 2a). It is likely that the anthraquinonesulfonic acid portion of the structure is conserved since it is, in part, responsible for its classification as an acid dye. The proposed structure differs from the Colour Index structure by replacing the acetamide group on the para position of the benzene ring with a methoxy group (Figure S1). The monoisotopic mass and isotopic distribution of the proposed structure (red circles in Figure 2a and 2b inlay) correlate with the observed mass and isotopic distribution from direct infusion ESI and MALDESI analyses within -0.98 and -1.6 ppm respectively. Also, the proposed structure is more likely to produce a neutral loss of a methyl group when fragmented. Peaks which correlated with nylon polymer were observed in the MALDESI analysis (green squares in Figure 2b). The destruction to the fabric was rather minimal, with a few fibers that were visibly melted (Figure 2c). Some of the top fibers of the weave were shredded, but most of the fibers in that section of the weave were not affected at all by the laser. The remaining fabric surface is untouched and as undamaged as prior to analysis.

The analysis of Acid Green 16 in nylon also resulted in an experimental mass of the $[\text{M}-2\text{H}]^-$ ion that did not match the theoretical monoisotopic mass of the main structure provided by the Colour Index (Figure S3a). It should be noted that this dye contains a quaternary ammonium cation which is why the loss of two protons gives an overall charge of -1 . However, the observed mass was greater than what the given structure indicated it should be. The experimental mass was 593.1793 but the monoisotopic mass is supposed to be 537.1159, a mass difference of 56.0634. Acid Green 16 was then analyzed using high resolving power mass spectrometry and MS/MS in negative ion mode to elucidate the structure. Performing sulfur and carbon counting on the high resolution experimental data indicated that the structure contains two sulfurs and about 30 carbons. The fragmentation of the ion at 593 resulted in a major fragment ion at 513.2218 (loss of 79.9568) and two minor fragment ions at 549.1166 (loss of 44.0620) and 469.1510 (loss of 124.0205) (Figure S3c). The major fragment at 513 corresponds to a loss of a sulfonic acid which is a possible fragment based on the expected structure. However, the minor loss at 549 (C_3H_8) does not match the Colour Index structure. The fragment ion at 469 resulted from a loss of a sulfonic acid and C_3H_8 . A new structure was proposed for this dye as well to match the accurate mass, fragmentation patterns, and carbon and sulfur counting (Figure S2a). The proposed structure differs from the Colour Index structure by replacing both dimethylamines with diethylamines. The monoisotopic mass and isotopic distribution of the proposed structure (red circles) matched the observed masses from the direct infusion ESI and MALDESI analyses (Figure 3b inlay), as shown in Figure S2a and the inlay in Figure S2b, with mass accuracies of -0.11 and 1.7 ppm respectively. The loss of C_3H_8 from the proposed structure is possible by the sequential loss of C_2H_5 and CH_3 which has been demonstrated to be a common fragment for diethyphenylammonium ions.²⁴ After further investigation it was discovered that both the proposed structure and the structure given by the Colour Index are possible structures for Acid Green 16. As with the other nylon fabrics analyzed by

MALDESI, the fabric was not shredded completely through (Figure S2c). Only the top few fibers of the threads in the weave were damaged. The remaining fabric surface was undamaged.

Basic Violet 16 was detected in positive ion mode from the acetate fabric as $[M]^+$. The mass of the dye from the MALDESI experiment (333.2325) corresponded to the theoretical monoisotopic mass (333.2325) with a mass accuracy of -0.075 ppm. The plot of the theoretical distribution (red circles) over the direct infusion ESI (Figure S4a) and MALDESI (Figure S4b) spectra also corroborates the accuracy of the match. In order to demonstrate its accuracy, the carbon counting technique was used to predict the number of carbons in the basic violet 16 structure where the theoretical mass matched the observed mass. This technique predicted around 22–23 carbons which correlates with the expected structure which has 23 carbons. There was very little observable damage caused by the laser after the MALDESI analysis of the acetate fabric (Figure S4c). On the “after MALDESI” overall fabric image, the damage is visibly undetectable. Even when looking closely at the microscopic image of the blast site, only a few fibers are cut and show the melted beads indicative of the laser's shots.

Disperse Red 60 in polyester was also detected in positive ion mode as $[M+H]^+$ with an observed m/z that corresponded to the theoretical mass with a mass accuracy of 0.63 ppm. The overlay of the theoretical distribution (red circles) on the direct infusion ESI (Figure S5a) and MALDESI (Figure S5b inlay) spectra corroborate the match. The polyester was even less damaged than the Basic Violet 16 acetate (Figure S5c). There is no visible destruction to the fabric on either the whole fabric overview or the specific image of the blast site. The “after” image of the polyester looks just as undamaged as the “before” image.

Along with dyed fabrics, fabric prints were also analyzed by MALDESI. The fabric print was pasted on 100% bleached cotton using a paste comprised of a binder, a thickener, and the pigment red 2b (146) dye. During the mass spectrometric analysis of the prints, a highly abundant polyethylene glycol (PEG) signal out-competed the signal from the pigment dye. To isolate the source of the PEG, the pigment dye and the un-pigmented print paste (just the binder and thickener) were separately analyzed and it was determined that a majority of the PEG signal was coming from the thickener. In an attempt to reduce the PEG saturation, the prints were washed with a surfactant and water at 160° F. The entire washing and drying process took roughly 30 minutes (5 minute wash and 25 minute to dry). When the prints were analyzed again, the polyethylene glycol levels were decreased by a significant amount, allowing pigment red 146 to be detected in positive ion mode as $[M+H]^+$, although in low abundance (Figure S6a). Figure S6b, a zoom in portion of the spectra in Figure S6a, shows the isotopic distribution of the dye with an overlay of the theoretical distribution (red circles).

There were a few dyes that were not detected by the direct analysis. However, it was not only when using MALDESI as a source that they were undetectable; the dyes not observed with MALDESI also could not be observed by direct infusion ESI, the contemporary source typically used. Most of the undetectable dyes are ionizable, except Vat Orange 7 and indigo, so it is unclear why this was the case. The dyes that were not detected include Acid Red 186 (nylon), Disperse Blue 79 (polyester), Indigo/Pigment Blue 66/Vat Blue 1 (cotton), Vat Orange 7 (cotton), Direct Red 24 (cotton and mercerized cotton), Reactive Red 141 (cotton), Reactive Blue 160 (cotton), Reactive Yellow 84 (cotton), and Pigment Red 112 (bleached cotton after washing). The structures and exact masses for these ions are shown in Table S2. Adding a few drops of an aqueous extraction solvent that was appropriate for the dye and fabric in place of just water as the matrix just prior to MALDESI-mass spectrometric analysis was also tried. While this approach was helpful for increasing the signal to noise of

the dye ions that were previously detected, those that were undetected using water as a matrix also went unobserved when using the extraction solvent.

CONCLUSION

MALDESI-MS has been demonstrated as an effective technique for the direct analysis of dyes from dyed textile fabric with minimal sample pretreatment. Compared to the more contemporary approach of dye extraction followed by either direct infusion ESI or LC-MS, this direct analysis approach provides similar spectral information about the dye (and fiber polymer in some cases) but in a significantly shorter period of time. Another benefit to the direct analysis is that the destruction to the fabric was minimal if present at all. The nylon displayed the most destruction, but even this damage was very small. The polyester showed almost no damage, and the acetate (viewed microscopically) did not show any damage at all. As a future consideration, the analysis of a single fiber or thread and fibers dyed with multiple dyes will be analyzed using MALDESI as a source since these conditions are more applicable to forensic cases.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Mass spectra and microscopic images of Acid Black 58 in nylon. (a) Mass spectrum of Acid Black 58 from direct infusion ESI, with the theoretical isotopic distribution (red circles). (b) Full scan mass spectrum from direct analysis of the dyed fabric by MALDESI with the dye peak (blue triangle) and nylon peaks (green squares) labeled. The inset shows a zoomed portion of the most abundant dye peak (blue triangle) with the theoretical isotopic distribution (red circles). (c) Dye structure as given by the Colour Index International and microscopic images of the dyed fabric before and after MALDESI analysis. The white square indicates the analyzed section displayed in the “after” image.

Figure 2.

Mass spectra and microscopic images of Acid Blue 40 in nylon. (a) Mass spectrum of Acid Blue 40 from direct infusion ESI, theoretical isotopic distribution (red circles) and the proposed structure based on accurate mass and MS/MS fragmentation. The inset shows the resolution of the ^{34}S and $^{13}\text{C}_2$ contributions to the A+2 peak. (b) Full scan mass spectrum from direct analysis of the dyed fabric by MALDESI with the dye peak (blue triangle) and nylon peaks (green squares) labeled. The inset shows a zoomed portion of the dye peak (blue triangle) with the theoretical isotopic distribution (red circles). (c) The proposed dye structure based on accurate mass, isotopic distribution, and MS/MS fragmentation as well as microscopic images of the dyed fabric before and after MALDESI analysis. The white square indicates the analyzed section displayed in the “after” image.