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Direct analysis of textile dyes from trace fibers by automated microfluidics extraction system coupled with Q-TOF mass spectrometer for forensic applications

Nadia Sultana[a], Sean Gunning[b], Stephen J. Furst[b], Kenneth P. Garrard[b], Thomas A. Dow[b], Nelson R. Vinueza[a,*]

[a] Department of Textile Engineering, Chemistry, and Science, North Carolina State University, Raleigh, NC 27695, USA
[b] Precision Engineering Consortium, North Carolina State University, Raleigh, NC 27695, USA

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ABSTRACT

Textile fiber is a common form of transferable trace evidence at the crime scene. Different techniques such as microscopy or spectroscopy are currently being used for trace fiber analysis. Dye characterization in trace fiber adds an important molecular specificity during the analysis. In this study, we performed a direct trace fiber analysis method via dye characterization by a novel automated microfluidics device (MFD) dye extraction system coupled with a quadrupole-time-of-flight (Q-TOF) mass spectrometer (MS). The MFD system used an in-house made automated procedure which requires only 10 μL of organic solvent for the extraction. The total extraction and identification time by the system is under 12 min. A variety of sulfonated azo and anthraquinone dyes were analyzed from ~1 mm length nylon fiber samples. This methodology successfully characterized multiple dyes (≥3 dyes) from a single fiber thread. Additionally, it was possible to do dye characterization from single fibers with a diameter of ~10 μm. The MFD-MS system was used for elemental composition and isotopic distribution analysis where MFD-MS/MS was used for structural characterization of dyes on fibers.

1. Introduction

Textiles fibers are the most common pieces of evidence found at a crime scene. Several techniques are being used to examine and discriminate one fiber from another [1]. Dyed trace fibers are differentiated using techniques such as microscopic, spectroscopic and spectrometric methods [1,2]. Ultraviolet-visible microspectrophotometry, confocal and infrared microscopy provide physical information such as birefringence, refractive index, luster and basic colorant information about the fibers [3–5]. Although these techniques provide important information about fiber types and basic colors, in some instances they lack molecular specificity and elemental composition information of dyes in the fibers that are crucial for forensic fiber analysis [2].

A common technique used to identify and analyze dyes from trace fibers is liquid chromatography (LC) and the main identification criteria of dyes using LC (coupling with diode array detector) are the absorption maxima and retention time. However, in some cases, the results obtained when two fiber were compared by these two (absorption maxima and retentions time) can be similar and cannot be individualized. For this reason, LC is combined with mass spectrometry (MS) to provide a better identification of the dye present in the trace fiber [1,6–9].

Direct analysis of the dyes on the fibers by using mass spectrometry is a new promising technique [2,10,11]. Tuinman et al. [10] carried out trace fiber color discrimination by the conventional extraction method followed by direct infusion to triple quadrupole mass spectrometer equipped with electrospray ionization source. The authors suggested that due to the low resolution of ESI-MS data, additional ESI-MS/MS is useful for identification that is more accurate. In the same way, several previous studies also demonstrated the applications of MS/MS for structural elucidation of the small molecules such as dyes. Based on these studies, specific organic functional groups and substituents can be correlated to their fragmentation patterns for structure analysis of the unknown compounds [12–17]. Both of these methods can be supplemented by database searching for mixtures of known and unknown compounds [2].

As a direct dye analysis method on fibers, Cochran et al. [2] utilized high resolving power mass spectrometer coupled with a

* Corresponding author.
E-mail address: nrvinuez@ncsu.edu (N.R. Vinueza).

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matrix-assisted laser desorption electrospray ionization (IRMALDESI) source, but the sample size they used (1 cm × 1 cm fabric) was bigger than the trace evidence usually found at a crime scene [1,2]. Following their previous work, Cochran et al. [18] were able to perform dye analysis from a single fiber via IRMALDESI imaging. During the analysis, single fibers remained on the ESI emitter, causing carryover. The authors suggested that further optimization of geometric parameter could eliminate this problem. Although this study focused on direct dye characterization from fibers without extraction method, traditional forensic fiber analysis consists of lengthy extraction methods, which leads to evidence loss [19]. For this reason, an easy and automated extraction methodology is needed that can facilitate the extraction, identification, and analysis of dyes on trace fibers.

In this study, we presented a direct analysis technique of textile dyes from trace fiber threads and single fibers through an automated microfluidics extraction system coupled to a quadrupole-time-of-flight (Q-TOF) mass spectrometer for forensic applications.

2. Materials and methods

2.1. Reagents and sample preparation

The solvent acetonitrile (LC–MS grade, 99.9%), isopropyl alcohol (HPLC grade,≥99.8%), and pyridine (ACS grade, 99.9%) were obtained from Fisher Scientific. Methanol (LC–MS grade, ≥99.9%) was purchased from J.T. Baker. The textile dyes were commercially available and their commercial sources and chemical information are shown in Table 1. Fig. S1 shows the chemical structures of all dyes. Woven raw nylon fabric (Type 306, Nylon 6.6) was purchased from Testfabrics, Inc.

For the preparation of dyed samples, raw nylon fabrics were dyed at 1% on weight fabric. The following dyeing procedure was performed: an aqueous stock solution (1 mg/mL) of the commercial dye was diluted to make a 300-mL dyebath for dyeing at 1% on weight of fiber on 3.00 g nylon 6.6 and then acidified to pH 4 by using glacial acetic acid. The dye and fabric were then placed into beakers and inserted into the Pyrotec MB2 (Roaches, UK) dyeing machine. The dyebath was heated to 100 °C at a ramp rate of 4 °C/min and was held at that temperature for 60 min. Dyed fabrics were then rinsed with cold water and dried at room temperature.

Fibers were pulled from the edges of the dyed fabric samples. Samples were prepared by cutting the fiber threads and single fibers using micropuncher (TED PELLA, INC.). The 2 mm fiber threads were cut in half. One part was kept as control (not extracted) sample and another part was extracted by the MFD system. The after extracted and the control fiber threads were placed under the microscope for visual inspection and photo capture. The length and width of the individual thread and diameter of single fibers were calculated from photographs (total magnification: 40×). These photographs were acquired using a Nikon Eclipse 50i POL Bright-Field microscope and analyzed using ImageJ software. Additionally, multiple threads (extracted and control samples) were photographed using Nikon SMZ1000 Zoom Stereomicroscope (total magnification: 8×) and the single fibers in the microfluidic cavity were photographed using Nikon SMZ800 Zoom Stereomicroscope (total magnification: 10×). Both stereomicroscopes had two coaxial illuminants for bright field observation.

2.2. Automated microfluidic dye extraction system

The microfluidic device (MFD) is an in-house made automated dye extraction system [19]. The MFD box is 9″ × 10″ × 7″ and weighs 10 lbs. It is an automated system powered by a single microprocessor and run through in-house-programmed software to control the extraction parameters. The MFD system consists of a removable extraction chamber, which is made from flexible perfluoro elastomeric (FFKM) material housed in a plastic (polyether ether ketone, PEEK) microfluidic chip (Fig. 1a and b). The extraction chamber contains a post that presses the fiber against the glass cover to hold it in the center of the cavity. A small frit (2μ porosity) is placed in the sample outlet to prevent any clogging of the lines.

MFD system simply requires the forensic examiner to place the fiber sample in the extraction cavity, close the glass cover, and insert the chip into the system (Fig. 1a and b). The MFD system then uses an automated sequence for the extraction of dyes (Fig. S2). The sequence includes multiple flushes at the end to increase dye extraction and ensure all residual dye has been removed from the cavity. Additionally, a cleaning sequence between each extraction assures no carryover. A detailed explanation of the automated sequence is described below.

2.2.1. Sealing the cavity

After inserting the microfluidic chip into the system, it is detected by an optical sensor. This triggers the system to extend a pneumatic cylinder. A heater assembly is connected below the pneumatic cylinder, which presses the chip's glass cover and seals the extraction cavity (Fig. 1c).

2.2.2. Extraction

The extraction is initiated by pushing the solvent (10 μL, pyridine/water = 4:3) from the reservoir to the MFD cavity via pneumatic pressure [19]. Once the cavity has filled with solvent, the heater increases the temperature of the cavity and solvent to 80 °C over 30 s. This temperature is maintained for 300 s to facilitate extraction.

Table 1
The dye standards used for the analysis.

No.	C.I name	Chemical class	Commercial sources	Chemical formula	Molecular weight (Da)
1	Acid Orange 7 (AO7)	Mono azo	Du Pont	$C_{16}H_{12}N_2O_4S$	328.34
2	Acid Yellow 199 (AY199)	Mono azo	M. Dohmen	$C_{19}H_{16}N_4O_6S$	428.42
3	Acid Yellow (AY219)	Dis azo	CIBA-GEIGY	$C_{20}H_{18}N_4O_5S$	426.45
4	Acid Red 266 (AR266)	Mono azo	M. Dohman	$C_{17}H_{11}ClF_3N_3O_4S$	445.80
5	Acid Red 337 (AR337)	Mono azo	DyStar	$C_{17}H_{12}F_3N_3O_4S$	411.36
6	Acid Red 361 (AR361)	Mono azo	CIBA-GEIGY	$C_{23}H_{26}N_4O_6S_2$	518.60
7	Acid Blue 113 (AB113)	Dis azo	MILES	$C_{32}H_{23}N_5O_6S_2$	637.69
8	Acid Blue 25 (AB25)	Anthraquinone	Aakash Chemicals	$C_{20}H_{14}N_2O_5S$	394.40
9	Acid Blue 40 (AB40)	Anthraquinone	Mobay Chemicals	$C_{22}H_{17}N_3O_6S$	451.45
10	Acid Blue 62 (AB62)	Anthraquinone	ICI Americas	$C_{20}H_{20}N_2O_5S$	400.45
11	Acid Blue 277 (AB277)	Anthraquinone	CIBA-GEIGY	$C_{24}H_{23}N_3O_8S_2$	545.58
12	Acid Blue 129 (AB129)	Anthraquinone	Sandoz Chemicals	$C_{23}H_{20}N_2O_5S$	436.48
13	Acid Blue 80 (AB80)	Anthraquinone	Polar Blue	$C_{32}H_{30}N_2O_8S_2$	634.72
14	Acid Blue 92 (AB92)	Mono azo	Anazolene Sodium	$C_{26}H_{19}N_3O_{10}S_3$	629.63