Spectra 3: Differentiation with Sample (C-60335 v. C-60344)

The Differentiation of Macroscopically Similar Black Fibers through Characterization of Nylanthrene Dyes using UV-Visible Microspectrophotometry and Thin Layer Chromatography

Andra D. Lewis, M.S.F.S.,[1] Chris Palenik, Ph.D., [2] Skip Palenik, B.S.,[2] and Patrick Buzzini, Ph.D.[1]

[1]Department of Forensic Science, Sam Houston State University, 1003 Bowers Blvd., Huntsville, TX 77340

[2]Microtrace LLC, 790 Fletcher Drive, Suite 106, Elgin, Illinois 60123

MEMBER THE TEXAS STATE UNIVERSITY SYSTEM

Microtrace LLC

INTRODUCTION

- Microspectrophotometry (MSP) is utilized in the forensic examination of trace evidence for the objective evaluation of color which is one of the most important discriminating characteristics of fibers. Microspectrophotometers can be used to measure color characteristics in the transmission, reflectance, or fluorescence of microscopic materials in the visible, the ultraviolet (UV) and near-infrared (NIR) regions. It has proven particularly advantageous when used in the differentiation of dyed fibers having a similar color.
- Visible MSP has been widely applied to the analysis of color increasing the discriminatory capabilities over light microscopy. However, auxiliary MSP methods have shown the potential to increase the discriminatory capabilities of the method, including the contributions of the short UV spectral range and of dichroism by means of plane-polarized light (PPL) microscopy.
- The goal of this study was to evaluate the various conditions of MSP to characterize and differentiate a reference collection of fourteen black fabric swatches dyed with known concentrations of four nylanthrene dyes – nylanthrene black GLWC, nylanthrene rubine SBLF, nylanthrene navy LFWG and nylanthrene orange SLF. Each fabric swatch contained either one, two, or three of the four potential dyes with a total dye concentration of 4% in each swatch.
- Fiber samples are a polyamide (nylon 6-6) primarily with a round cross section. The nylanthrene dyes, which are no longer produced, were known for their favorable migration properties which provided excellent coverage as well as stain resistance. Besides known dye variations, the fabric swatches were macroscopically indistinguishable to each other, thus requiring deeper investigation.
- The ability to increase the discriminatory capabilities of MSP by examining single fiber specimens in the UV range provides better structural information and the ability to accurately discriminate between similar dyes.
- The ability to increase the discriminatory capabilities of MSP by examining dichroism is also an important consideration as shown by De Wael et al., (2011, 2012). When a clear dichroic effect is observed with PPL microscopy, the additional benefit of using MSP lies in the fact that a correspondence or a difference in the dichroic behavior of fiber specimens and reference can be measured in an objective way. In specimens which are composed of different dye mixtures, very similar absorption spectra in the visible range are obtained by MSP with non-polarized light. Using MSP-PPL, differences in the dichroic behavior of one of the dyes may lead to differences in the spectra.
- Colorants are added to both man-made and synthetic fibers to make them commercially more useful and may be a single component or a mixture of dyes.
- Thin layer chromatography (TLC) is an analytical technique which allows the constituent components of dyes to be separated and thus allows for the ability to compare dyes extracted from fibers.

MATERIALS AND METHODS

Materials:

- The Nylanthrene Black Reference Grid by the Crompton and Knowles Corporation was used in this study as a known reference (see Figure 1 below).

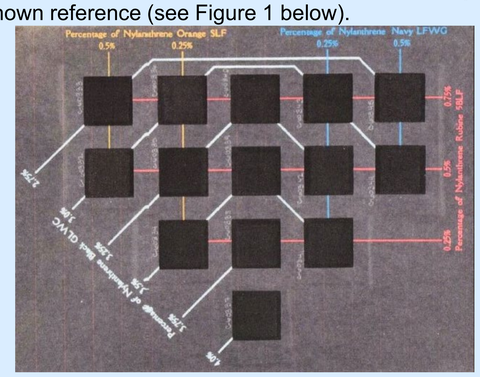


Figure 1: Fourteen black fabric swatches dyed with known concentrations of nylanthrene dyes

Microscopical Analyses:

- The fiber samples were a polyamide (nylon 6-6) dyed with known concentrations of 4 different nylanthrene dyes which appeared macroscopically similar in color (black).
- Microscopical examination revealed a round cross-section and peculiar dye properties. The fibers exhibited a lighter color (orange-red-brown) in the center, with the edges of the fibers exhibiting a darker color (blue gray/green blue).

Figure 2: Cross-section and analysis of fiber in horizontal and vertical positions

UV-VIS Microspectrophotometry:

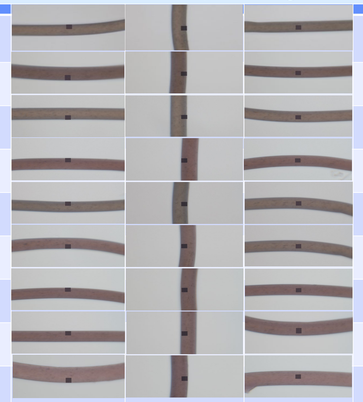
- Three fibers from each indistinguishable sample (9 samples total) were examined within the UV-Vis spectral range of 300 – 700 nm (see figures 3 – 6).
- Six locations per fiber were analyzed in the horizontal and vertical position with and without a polarizer.

Dye Extraction and TLC

- The dye was extracted from the polyamide fibers using a mixture of pyridine/water (4:3) at 100°C for 20 minutes.
- Dye extracts were spotted 1cm from the base of the TLC plate and eluted with n-butanol, ethanol, ammonia and pyridine (4:1:3:2). All samples were eluted in duplicate (see figures 7 and 8).

RESULTS

Table 1: Classification of Black samples using microscopy and UV-Vis MSP

Sample	Dye Description		Microscopy	UV-Vis MSP
C-60334	3.5% Nyl. Black 0.25% Nyl. Rubine 0.25% Nyl. Orange		Unable to distinguish from samples C-60338 and C-60341	Able to distinguish from samples C-60338 and C-60334
C-60335	3.25% Nyl. Black 0.50% Nyl. Rubine 0.25% Nyl. Orange		Unable to distinguish from samples C-60339 and C-60344	Able to distinguish from samples C-60339 and C-60344
C-60338	3.75% Nyl. Black 0.25% Nyl. Rubine		Unable to distinguish from samples C-60334 and C-60341	Unable to distinguish from sample C-60334; able to distinguish from sample C-60341
C-60339	3.50% Nyl. Black 0.50% Nyl. Rubine		Unable to distinguish from samples C-60335, C-60341 and C-60345	Unable to distinguish from sample C-60341 and C-60345; able to distinguish from sample C-60335
C-60341	3.50% Nyl. Black 0.25% Nyl. Rubine 0.25% Nyl. Navy		Unable to distinguish from samples C-60334 and C-60338	Able to distinguish from samples C-60334 and C-60338
C-60342	3.25% Nyl. Black 0.50% Nyl. Rubine 0.25% Nyl. Navy		Unable to distinguish from sample C-60339	Unable to distinguish from sample C-60339
C-60343	3.00% Nyl. Black 0.75% Nyl. Rubine 0.25% Nyl. Navy		Unable to distinguish from sample C-60345	Unable to distinguish from sample C-60345
C-60344	3.00% Nyl. Black 0.50% Nyl. Rubine 0.50% Nyl. Navy		Unable to distinguish from samples C-60335 and C-60339	Unable to distinguish from sample C-60344; able to distinguish from sample C-60339
C-60345	2.75% Nyl. Black 0.75% Nyl. Rubine 0.50% Nyl. Navy		Unable to distinguish from samples C-60339 and C-60345	Unable to distinguish from samples C-60339 and C-60345

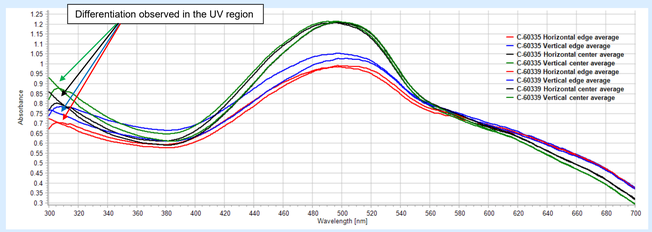


Figure 3: UV-Vis Spectra showing differentiation of Samples C-60335 v. C-60339

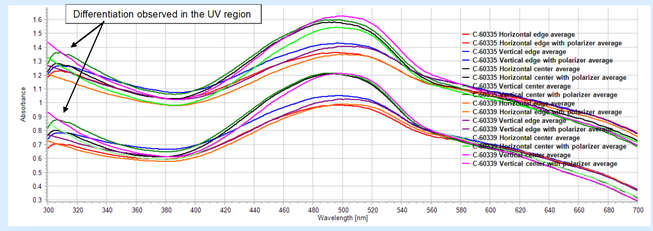


Figure 4: UV-Vis spectra showing differentiation of Samples C-60335 v. C-60339 with polarizer

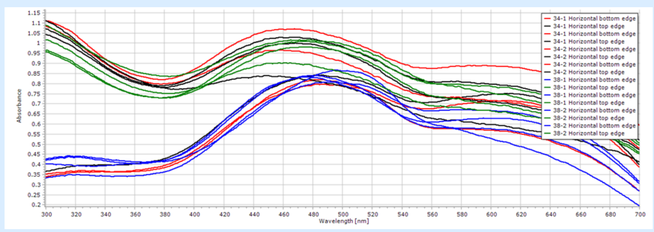


Figure 5: UV-Vis spectra showing similarity between Samples C-60334 v. C-60338

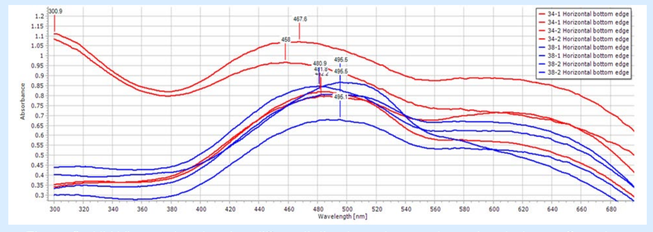


Figure 6: UV-Vis spectra showing differentiation based on peak maxima between Samples C-60334 v. C-60338

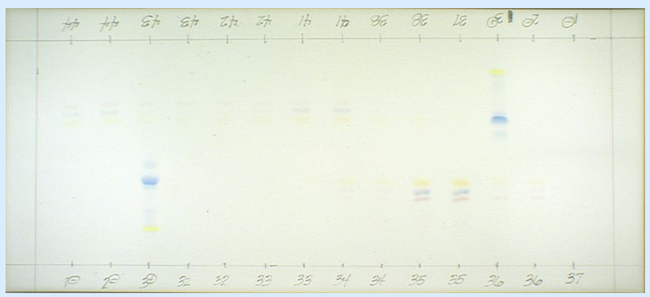


Figure 7: TLC plate of nylanthrene dyed fibers (white light)

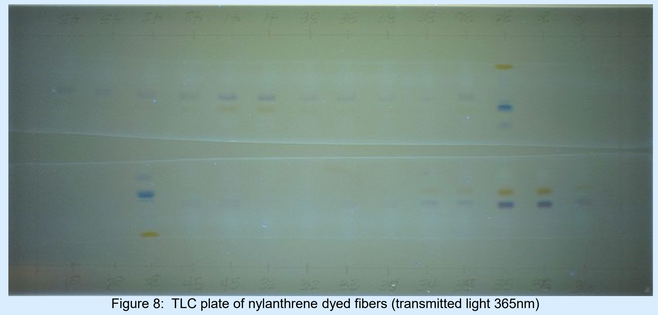


Figure 8: TLC plate of nylanthrene dyed fibers (transmitted light 365nm)

CONCLUSIONS

- After comparison microscopy, 9 pairs of samples were not able to be differentiated.
- After UV-Vis MSP, 5 pairs of samples were not able to be differentiated.
- The UV region of the MSP spectra showed distinct differences which allowed the differentiation of the samples.
- Thin layer chromatography (TLC) provided additional information which provided further discrimination.

ACKNOWLEDGEMENTS

I would like to thank Mr. Skip Palenik and Dr. Christopher Palenik for the opportunity to learn at Microtrace during the summer of 2019 where this study was initiated.

REFERENCES

- Biermann, T. W. (2007). Blocks of colour IV: The evidential value of blue and red cotton fibres. Science & Justice, 47(2), 68–87.
- De Wael, K., & Vanden Driessche, T. (2011). Dichroism measurements in forensic fibre examination: Part 1 — Dyed polyester fibres. Science & Justice, 51(2), 57–67.
- De Wael, K., & Vanden Driessche, T. (2011). Dichroism measurements in forensic fibre examination: Part 2 — Dyed polyamide, wool and silk fibres. Science & Justice, 51(4), 163–172.
- De Wael, K., Lepot, L., & Lunstroot, K. (2012). The use of linear dichroism in forensic fibre examinations — Part 6. Validation and practical aspects of MSP-PPL. Science & Justice, 52(4), 249–258.
- Grieve, M. C., Biermann, T. W., & Davignon, M. (2001). The evidential value of black cotton fibres. Science & Justice, (4), 245.
- Wiggins KG. Thin Layer Chromatographic Analysis for Fibre Dyes. In: Robertson J, Grieve M, editors. Forensic Examination of Fibres, 2nd edn. London, UK/Philadelphia, PA: Taylor & Francis, 1999: 291-309