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The mission of ASTEE is to encourage the exchange and dissemination of ideas and information within the field of trace evidence through improved contacts between persons and laboratories engaged in trace evidence analysis. The journal of the American Society of Trace Evidence Examiners is a peer reviewed journal dedicated to the analysis of trace evidence. All original articles published in JASTEE have been subject to double-blind peer review.

Inside This Issue

JASTEE has established a working relationship with the Scientific Working Group on Materials Analysis (SWGMAT); whereby approved SWGMAT standards maybe published in *JASTEE*. These standards have been peer reviewed and approved by the SWGMAT group as a whole and thus were not subject to peer review through *JASTEE*.

JASTEE has also established a working arrangement with *The Microscope*, the journal established and edited by the McCrone Institute. Under this arrangement, articles published in *JASTEE* may be selected for publication in *The Microscope*, and vice versa.

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Synthetic Wig Fibers: Analysis & Differentiation from Human Hairs

ABSTRACT

Due to their transferability, synthetic wig fibers have been encountered in forensic casework samples. Such samples may be submitted to laboratories as suspected human hairs, fibers, or known "head hair" samples. When submitted to the laboratory as suspected 'hairs', DNA suitability examinations and/or hair comparisons may be requested on these evidentiary samples. Therefore, this fiber evidence may find its way onto the bench of examiners with different backgrounds and training. This study explored the utility of analytical techniques to distinguish human hairs and wig fibers for examiners not trained in the recognition of fibers. This study also investigated an analytical scheme likely to be used by a fiber examiner analyzing wig fiber evidence. Different techniques were applied to a sample set of 62 wig fibers. At the conclusion of analysis, it was found that aspects of the analysis scheme could be used effectively by an examiner not trained in the recognition of fibers and that all but a few groups of the 62 wig fibers were distinguishable using the analytical scheme employed.

Keywords: Wigs, Wig fibers, Hairs, MSP, FTIR, Cross-sections, Scale casts, PLM, Microscopy

INTRODUCTION

Casework at the Minnesota Bureau of Criminal Apprehension (BCA) has indicated a rising occurrence of potential wig fibers submitted as "apparent hairs" for DNA testing and/or hair comparisons. Wigs have gained considerable popularity in the fashion and beauty market and remain very important for medically related reasons. Significant improvements in materials during the past decade have helped create synthetic hair with a more natural look and feel with some commercially available wigs able to withstand heat styling (1,2). Due to these improvements in wig manufacturing, it is likely that an increase in the number and variability of wig fibers will continue to appear in casework.

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Few studies have focused on the characterization of wig fibers (1,3,4). Based on the increased incidence of wig fibers submitted as evidence and the paucity of research regarding these fibers, the aim of this study was to examine the utility of different techniques used in hair and fiber examinations for the analysis of wig fibers with the intent of evaluating whether some of these techniques could be useful in distinguishing a human hair from a wig fiber for scientists not trained in the recognition of fibers.

At the BCA Forensic Lab, this evidence is submitted to the Trace Evidence section for examination, but in other laboratories the "apparent hairs" could be examined by a biologist assessing the hair for DNA suitability. This research was conducted with consideration for the different training levels of the scientists possibly involved in such examinations. If a wig fiber is 'screened' for nuclear DNA suitability by an examiner not trained in the recognition of fibers, the fiber may be deemed not suitable for DNA analysis resulting in a loss of evidential value and potential fiber examinations. Furthermore, this study evaluated the discriminating power of the following techniques when applied during a fiber examination: Polarized Light Microscopy (PLM), cross-sections, Fourier Transform Infrared Spectroscopy (FTIR) and Visible Microspectrophotometry (MSP). PLM, FTIR and visible MSP are recognized instrumental techniques used for the analysis of textile fibers (3,4,5,6). Employing a combination of these techniques has been found to discriminate between textile fibers.

The results of this study showed that for a non-fiber examiner, some of the analytical techniques used could increase their ability to distinguish a hair from a wig fiber. This is particularly useful for cases in which the submitting agency has requested that the "hairs" be examined for DNA testing and/or microscopically compared. Furthermore, all but a few groups of fibers were distinguishable from each other using the techniques listed above.

MATERIALS AND METHODS

Fiber Collection

Wig fiber selection included collecting 62 fibers from 33 non-costume synthetic wigs from a local Merle Norman store. Information regarding brand/manufacturer was obtained from the wigs label during collection. All samples are listed in Table 1. Multiple wig fiber samples were collected to account for variation in macroscopic color. Wig fibers that exhibited color variation within the sample were further designated alphabetically. For example, sample 22 contained three different colored fibers designated 22A, 22B, and 22C.

Table 1. Wig Fiber Samples

Identifier	Brand	Collection/Model	Color	Material	Origin of Manufacture	Price
1	TressAllure by Revlon	1003586			USA, Florida	200
2	Motown Tress	Sabrina	1B	Kanekalon	China	45
3	Alicia Beauty	Leann 10505	2	Kanekalon	China	77.99
4	Bobbi Boss by Midway International	M174 Pinto	1		Indonesia	32.99
5	Motown Tress	Feather Lite FeeFee	1B			34.99
6	Bobbi Boss by Midway International	M216 Kristi	2		Indonesia	37.99
7	Raquel Welch by Hair U Wear	Signature Collection	Ginger Brown	100% Polyester	Japan/Indonesia	
8	Gabor by Hair U Wear	Cheer	Buttered Toast Mist	Kanekalon - Flexlite Modacrylic		110
9	Rene of Paris	Faye (2361)	Creamy Toffee		Both- Thailand	129.95
10	Gabor by Hair U Wear	Gambit	Buttered Toast Mist	Kanekalon - Flexlite Modacrylic	Wig- Indonesia, Modacrylic - Japan	
11	Simply Beautiful by Revlon	Snuggle	10-130TR Autumn Glow	Kanekalon - Spectrablend Modacrylic	Indonesia	
12	TressAllure by Revlon	Midnight	Chestnut	Kanekalon - Spectrablend Modacrylic	Wig- Indonesia, Modacrylic - Japan	179.99
13	Pierre	International Collection Feather Lite Mono (WBP-1018)	Honey Red	Monofilament Synthetic		229
14	Tony of Beverly	Lacey	12S28	Modacrylic		299
15	Estetica Designs	Cap Collection - Sapphire	R33/29/26			110
16	Gabor by Hair U Wear		Paprika Mist	Kanekalon - Flexlite Modacrylic		115
17	Raquel Welch by Hair U Wear	Signature Collection -Entice	Cinnabar R32/31	Kanekalon - Vibralite Modacrylic		129
18	Raquel Welch by Hair U Wear	Sheer Indulgence - Sorcery (SS130)	Dark Copper	Kanekalon - Vibralite Modacrylic		134
19	Rene of Paris	Amore Designer Series	Copper Glaze	Modacrylic	Wig -Thailand Modacrylic - Japan	
20	Rene of Paris		Copper Glaze	Modacrylic	Wig -Thailand Modacrylic - Japan	
21	Tony of Beverly		Red	Eurotex' Kanekalon Blend Modacrylic	Indonesia	
22	Gabor by Hair U Wear		Paprika Mist	Flexlite Modacrylic	Wig- Indonesia, Modacrylic - Japan	
23	Estetica Designs	High Society Collection		100% Modacrylic	Wig- Indonesia, Modacrylic - Japan	
24	Rene of Paris		Auburn Sugar	Modacrylic	Thailand	
25	Osolite by Jon Renau		Caramel Syrup	100% Modacrylic (Company- Kanekalon)	Wig- Indonesia, Modacrylic - Japan	
26	Jon Renau		Auburn	100% Modacrylic (Company- Kanekalon)	Japan	
27	Raquel Welch by Hair U Wear	Signature Collection	Midnight Brown	100% Kanekalon Vibralite		
28	Aspen		Coco	100% Modacrylic	Wig- China, Modacrylic - Japan	
29	Aspen	Imagination -			China	
30	Raquel Welch by Hair U Wear	Sheer Indulgence -		100% Polyester	Wig- Indonesia, Modacrylic - Japan	314
31	Rene of Paris	Noriko Collection	Coco Swirl	100% Modacrylic	Wig -Thailand Modacrylic - Japan	
32	Gemtress	Syntress Collection		100% Syntress Fiber		
33	Pierre	Angelina Lace Front (WBP-906)	Chestnut	100% Synthetic	Wig- Indonesia, Modacrylic - Japan	399

**All prices are in US $*

Stereomicroscopy/Polarized Light Microscopy (PLM)

Fibers from each sample were examined and photographed under low magnification (10X) using a Leica MZ16 Stereomicroscope. Samples were also mounted on clean microscope slides in Permount (refractive index 1.525). An Olympus BX51 PLM (100X –

400X magnification) was used to examine the microscopic characteristics of the wig fibers. These characteristics were documented using a PLM worksheet (Table 2).

Table 2. PLM Worksheet

Sample Number	Macroscopic Shape	Exterior Appearance	Diameter	Color	Middle Section	Other internal features- Delustrant, fish eyes, pigment, etc.	Retardation colors
	Straight ☐ Wavy ☐ Curly ☐	Smooth ☐ Disrupted☐		Black ☐ Brown ☐ Blonde ☐ Colorless ☐ Red ☐	Consistent☐ Inconsistent☐ Not present ☐	Present ☐ Abundance/ appearance Not present ☐	bright ☐ dull ☐ Gray/white ☐ None observed ☐

The macroscopic and microscopic characteristics used to describe each sample were also useful in categorizing the samples into distinguishable groups for the fiber discrimination portion of this study.

Scale Casting

Scale casts, not generally used for forensic fiber examinations, are a rudimentary method used primarily by hair examiners for visualizing hair scale patterns. Scale casts were made of selected fibers by placing a few thin layers of clear nail polish on a microscope slide followed by positioning the fiber flat in the nail polish. The nail polish was allowed to dry, after which the fiber was slowly removed, leaving an impression of the exterior of the fiber (7). The scale casts created from the wig fibers and a single human hair scale cast were examined side by side with 200X magnification and photographed using a SONY camera on an Olympus BX51 comparison microscope.

Cross -Sections

Cross-sectioning is a technique that is applicable in both textile examinations (5) and hair examinations, for determination of racial characteristics (8,9). Fibers were cross-sectioned in order to determine their shape. Cross-sections were made by placing the fiber into a small pipette tip with an appropriate amount of Norland Optical Adhesive 65. The adhesive was cured by exposing the pipette tip to ultraviolet light. While viewing with a Leica MZ16 stereomicroscope, a razor blade was used to cut small sections of the pipette tip portion including the fiber and adhesive. With each section, the surrounding pipette plastic was removed and the cross-sections were placed on microscope slides, photographed and examined by PLM.

Spectroscopy

Following cross-sections, FTIR spectroscopy was performed to examine the chemical composition of the fibers. A portion of each fiber was flattened on a microscope slide, transferred to a sodium chloride (NaCl) disk and analyzed in transmission mode using an Autoimage microscope attached to a Perkin Elmer Spectrum One spectrometer with a mercury cadmium telluride (MCT/A) detector (4000 cm^{-1} to 650 cm^{-1}). Sixteen scans were acquired at a resolution of 4 cm^{-1} with a 2 cm^{-1} interval. The above operating conditions are the BCA laboratory standard operating conditions for this instrument.

MSP was used to analyze the dyes in the sample set. A SEE 2100 Microspectrophotomer with a charge-coupled device (CCD) array detector, 15X objective, a 75 watt xenon light source for transmission in the visible range (400-750 nm), and a spectral bandwidth of 0.32 nm was used. A total of 10 scans were collected along the length of each fiber, including color variations that occurred within the fiber. The same mounted fibers examined by PLM were used for this analysis. MSP was not performed on colorless fibers as these do not provide an absorbance spectrum.

RESULTS AND DISCUSSION

Microscopy

The Stereomicroscope and Polarized Light Microscope were the first instruments used in the analytical scheme because, regardless of the level of training, some form of microscopy should be the first tool an examiner uses when a suspected "hair" is submitted as evidence (8,10,11). Using the PLM worksheet (Table 2) as a guideline, the macroscopic shape was examined with most fibers exhibiting a straight or wavy appearance. Under low power magnification, some samples exhibited hair-like characteristics and if in fragment form could possibly be mistaken as hairs. For the mounted samples, the external appearance or edges of the fiber were examined. Some fibers presented a rough exterior texture that could be confused with imbricate scale structure found in hairs. Diameter measurements were also made on the mounted samples. For human head hairs, the diameter variation has been reported to be between 55 μm and 100 μm (12) and the mean diameter reported to be 80 μm (13). Eighty-nine percent of the wig fiber samples had a diameter within the range of 55-100 microns. Eleven percent of the wig fiber samples had a diameter greater than 100 μm.

The retardation colors were examined and most of the fibers exhibited gray/white colors under crossed polars, with two fibers having no observable retardation colors. These two fibers were not isotropic but were simply too dark in color for the observer to characterize the colors while using the PLM worksheet (Table 2). Some fibers contained a middle section that could be misconstrued as a medulla, as well as a rough exterior texture and clear margins that resembled a cuticle. These are features which, if considered singularly, could contribute to a misclassification of a fiber as a hair. Internal features, such as delustrant and fish eyes, were also noted (Figure 1).

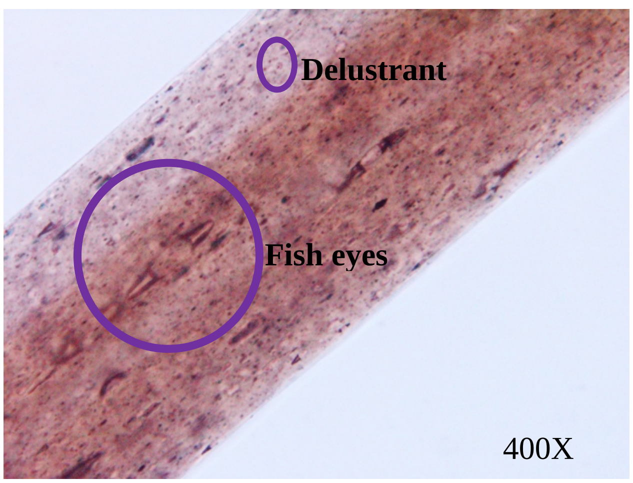


Figure 1 Photomicrograph which illustrates internal features of some fibers

Although delustrant is an internal feature which should be noted, it may be confused with ovoid bodies and/or cortical fusi observed in hair, to a non-fiber examiner. Therefore, the presence of fish eyes is more important in the discrimination between a fiber and a hair for non-fiber examiners. Fish eyes are created in the manufacturing process of synthetic fibers when undissolved polymer, pigment and other compounds are present during the drawing process (4).

The characteristics examined macroscopically and microscopically and recorded on the PLM worksheet (Table 2) were basic features that an examiner, regardless of training, could describe. To confirm the assertion that these features are generally recognizable, a student intern utilized the PLM worksheet during this project with only a brief explanation of hair and fiber characteristics. The intern was successful at using the worksheet as a guideline for recognizing the features which distinguish a human hair from a wig fiber.

Scale Casting

For the fibers in this study that lacked fish eyes, scale casts were made. Although limited by fiber length, a simple technique such as scale casting was chosen to aid in the discrimination of hairs and fibers and can be used by non-fiber examiners who do not observe fish eyes in an evidentiary sample (indicating a fiber). In all of the fiber scale casts, longitudinal lines were observed microscopically. Longitudinal lines were not present in the hair cast taken (Figure 2). Caution should be taken when examining the scale casts of highly processed hairs since they may be excessively damaged and lack a cuticle (14).

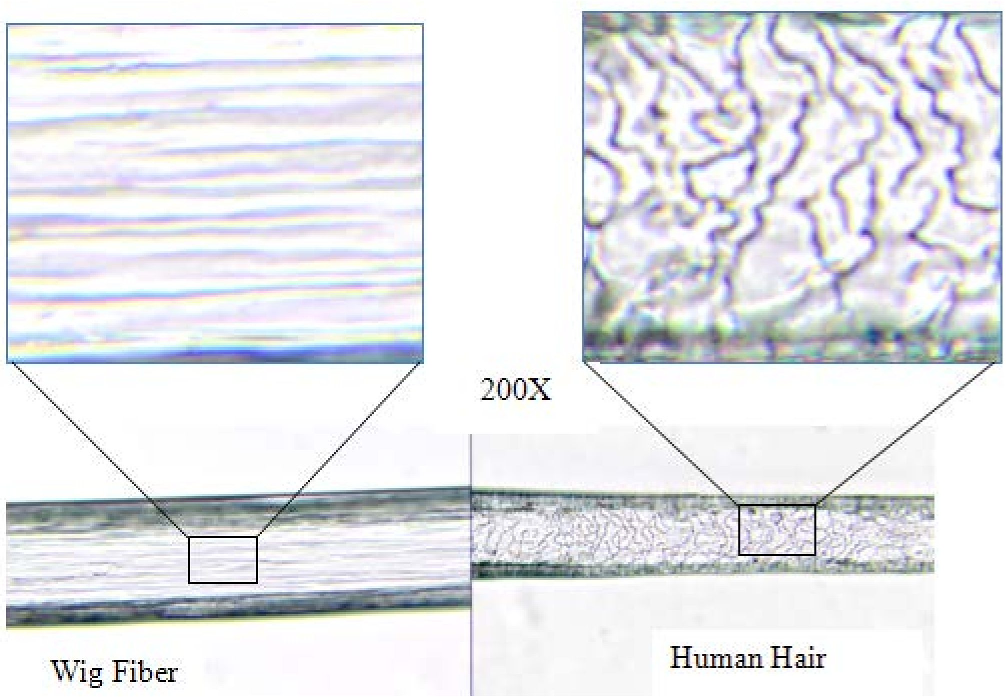


Figure 2 Hair vs. fiber magnified scale casts

Cross-Sectional Analysis

Within the test group of 62 fibers, 10 different cross-sectional shapes were observed. The cross-sectional shapes were defined as round, lobular (6 lobes), irregular lobular, ribbon, bean, horseshoe, U-shaped, plumped dogbone, folded ribbon, and plumped dogbone/bean (Figure 3). Hairs possess cross-sectional shapes that are typically oval, round, or flattened. Although limited by fiber length, the analysis of cross-sectional shape adds another distinguishing layer to fiber examinations and may also help an examiner distinguish fibers from hairs if they choose to employ this technique. Cross-sectional shapes are created during the manufacturing process and may be for aesthetic purposes, such as luster, dimension, and volume. The fiber cross-sectional shape may be intentional or a by-product of the spinning process. Spinning is the technique used to force the polymer through holes in a spinneret producing strands that are allowed to solidify. The dogbone cross-section of some acrylics, for example, is created during dry spinning when the round fiber collapses as the solvent is being evaporated in dry air (6).

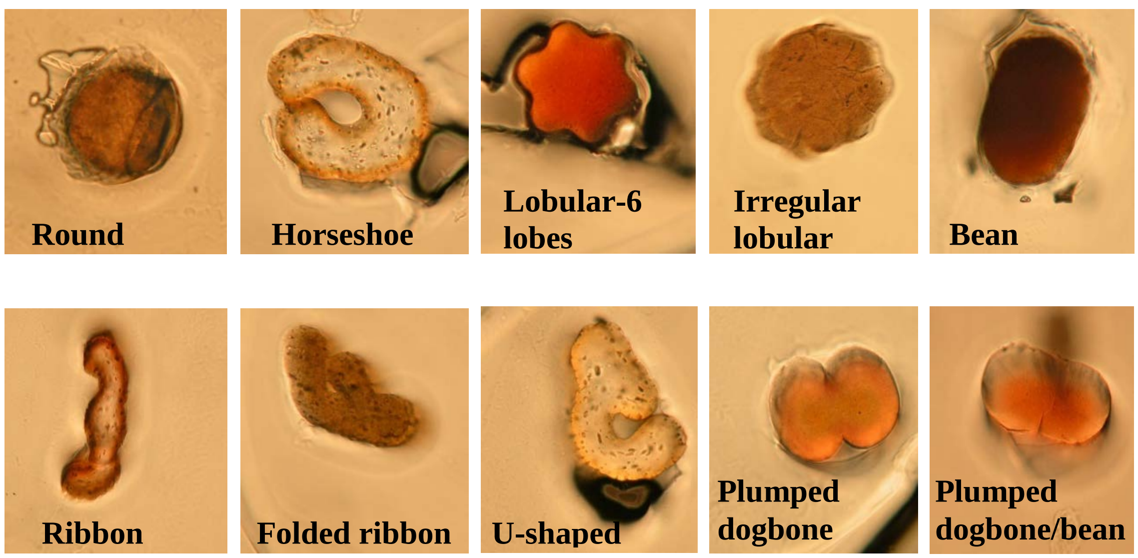


Figure 3 Photomicrographs of cross-sectional shapes magnified at 400X

Instrumentation

FTIR and MSP were utilized to investigate their discriminating power when applied to the wig fiber sample set for application by a fiber examiner. FTIR spectroscopy identified four fiber types within the sample set: polyester (polyethylene terephthalate (PET)), vinyon (polyvinyl chloride), modacrylic (polyacrylonitrile/vinyl chloride (PAN/VC)), and modacrylic (PAN/VC) with a solvent peak (acetone) at 1708-1710 cm^{-1} (4). The polyester FTIR spectrum had peaks at 1720 cm^{-1}, 1410 cm^{-1}, 1250 cm^{-1}, 1100 cm^{-1}, 1020 cm^{-1}, 730 cm^{-1}, and an important peak at 1340 cm^{-1}. The 1340 cm^{-1} peak helps identify the polyester type as PET, from other polyester types (Figure 4). For example, this peak is absent in polybutylene terephthalate (PBT) polyester.

The PAN/VC FTIR spectra showed a large 2242 cm^{-1} peak, a 1735 cm^{-1} peak that was 50% of the size of the 2242 cm^{-1} peak, and vinyl chloride co-polymer peaks at 1326 cm^{-1}, 1239 cm^{-1}, and 695 cm^{-1} (Figure 5). The other type of PAN/VC spectra included an additional peak at 1708 cm^{-1} (Figure 6). According to literature, this peak is acetone which is used as a solvent in the manufacturing process (4).

The vinyon FTIR spectrum had peaks at 2918 cm^{-1} and 1429 cm^{-1} and lacked the large 2242 cm^{-1} peak indicative of a carbon-nitrogen triple bond, C≡N (Figure 7).

Interestingly, some wigs contained multiple fibers with different chemical compositions. For example, sample 28 was found to contain both vinyon and PAN/VC fibers although it was obtained from a wig with a label indicating the material was 100% modacrylic. Kanekalon, a major wig manufacturer, explained that this blend is created for aesthetic purposes, style and color (personal communication with Kanekalon representative).

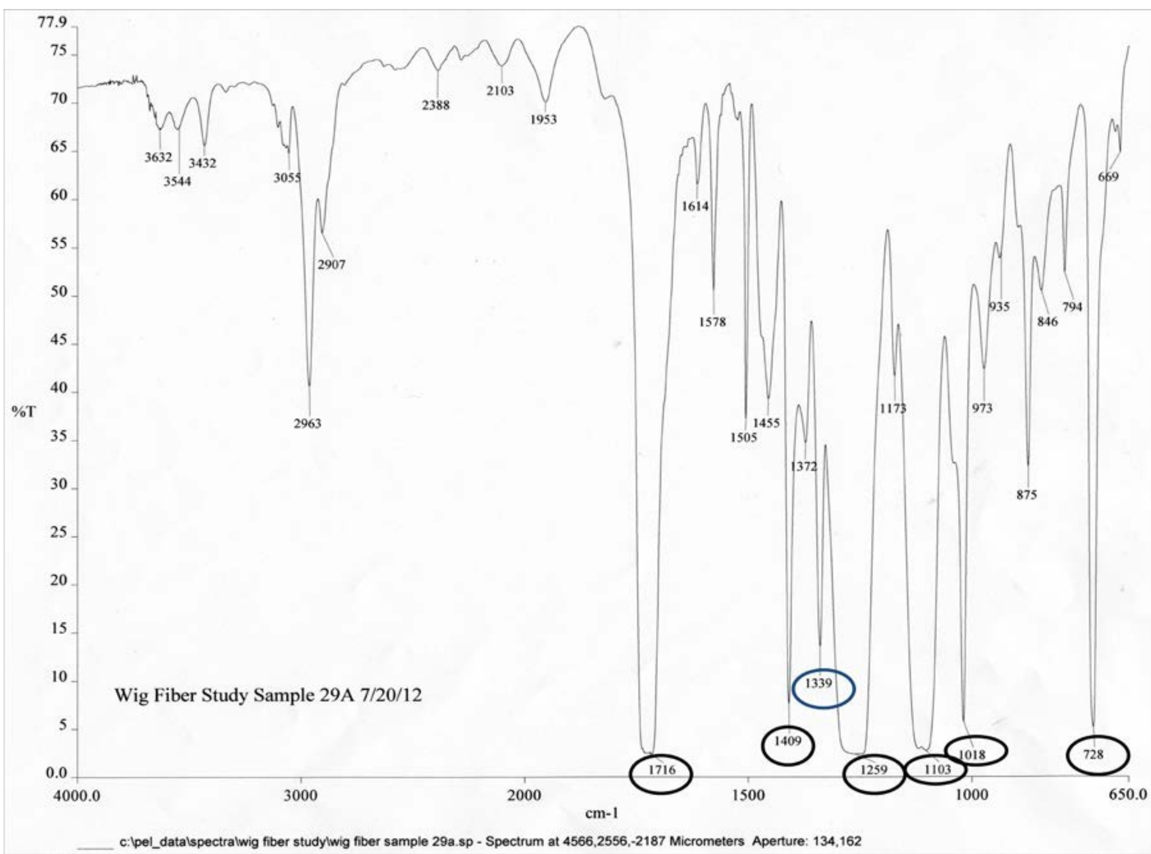


Figure 4 Polyester (polyethylene terephthalate) spectrum

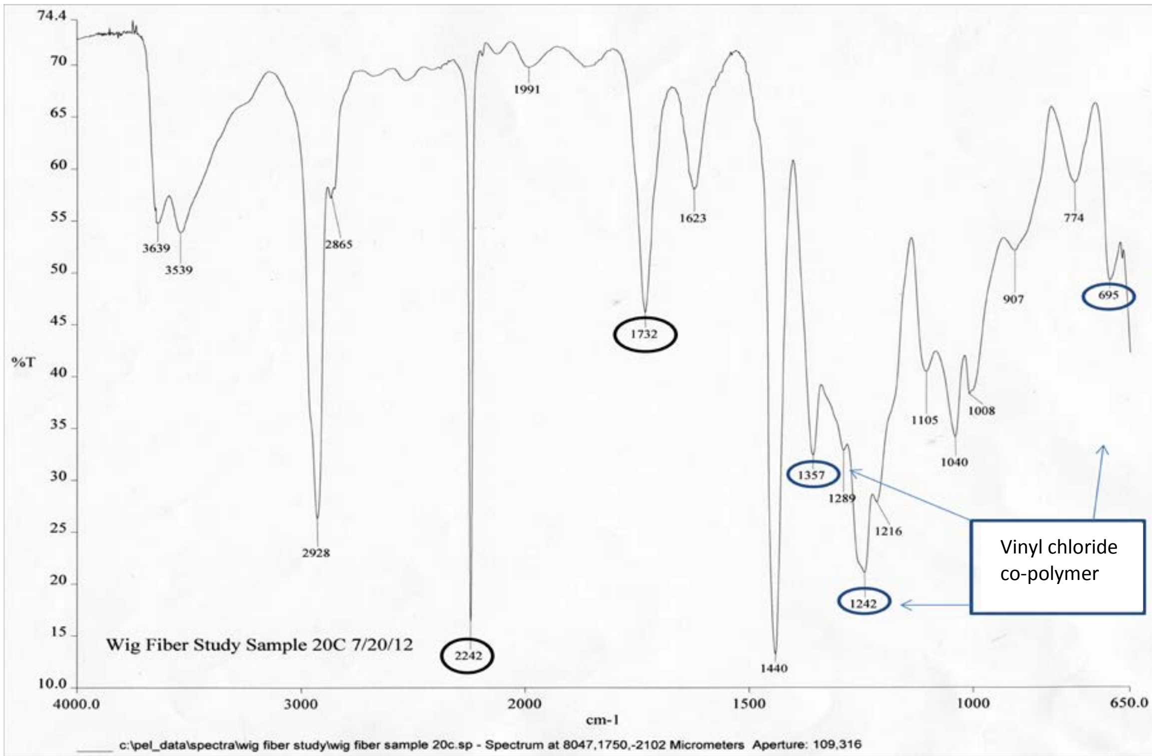


Figure 5 Modacrylic (polyacrylonitrile/vinyl chloride) spectrum

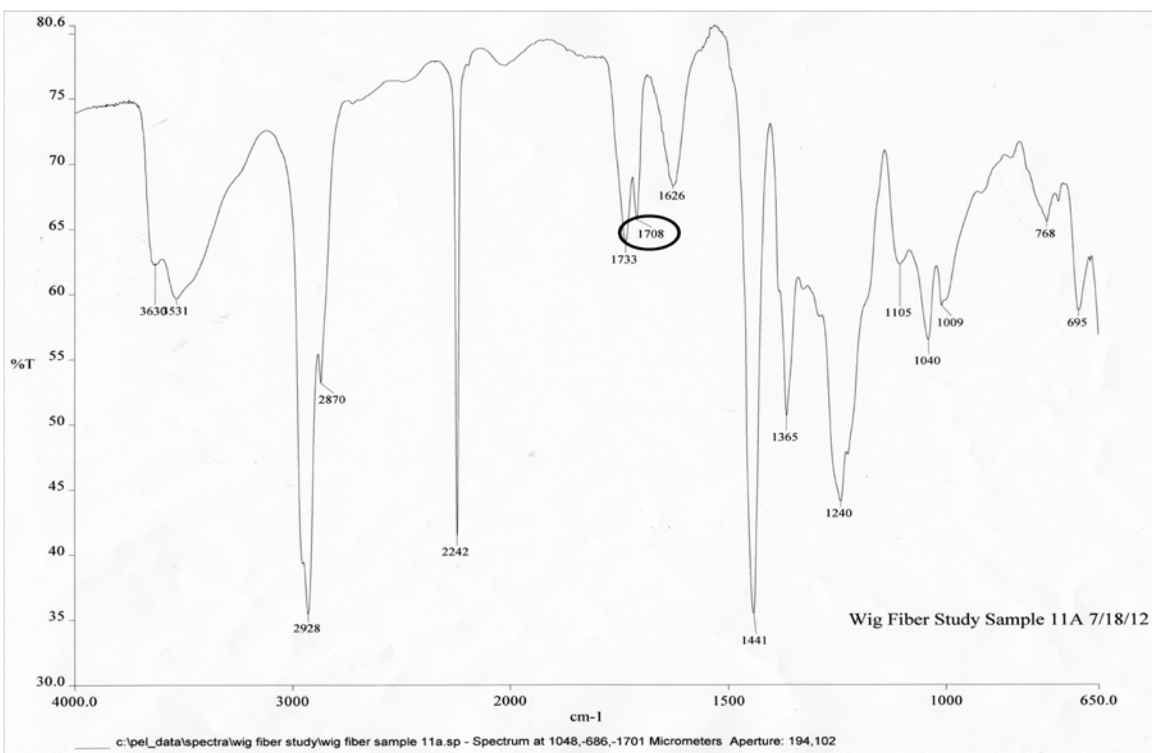


Figure 6 Modacrylic (polyacrylonitrile/vinyl chloride) spectrum with solvent peak

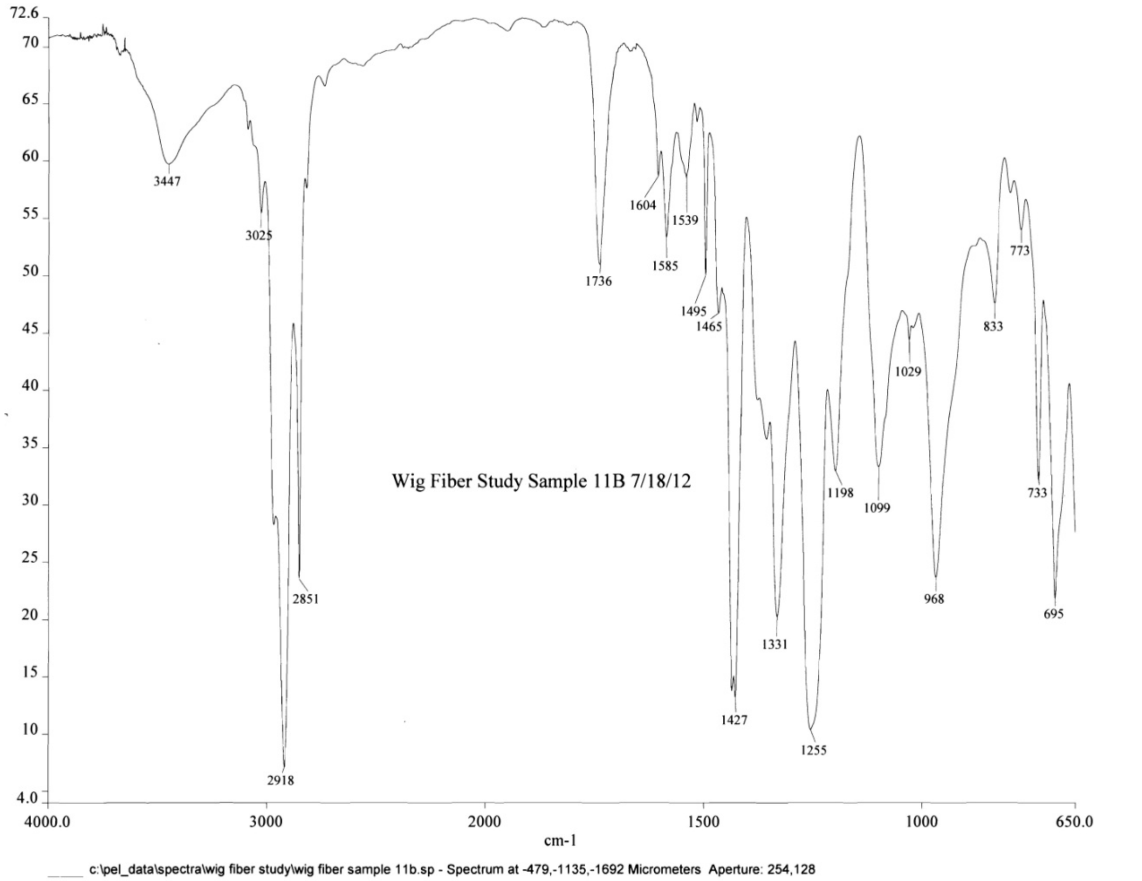


Figure 7 Vinyon

Fibers were distinguished by MSP based on differences in peak position, peak width, and slope. Although not all of the fibers were distinguishable by MSP, the results did provide support for the discriminating power of this technique when used for textile color analysis.

Discrimination of Fibers using Analytical Scheme

The data as a whole was evaluated to see if all the wig fibers in the sample set could be distinguished from each other based on the techniques utilized during this study and without the use of side-by-side comparison microscopy. Overall, out of the 62 fibers sampled, 36 (58%) fibers were distinguishable from all other wig fibers in this study. Figure 8 explains which fibers were indistinguishable after consideration of color, presence/absence of fish eyes, cross-sectional shape, infrared spectra, and visible spectra.

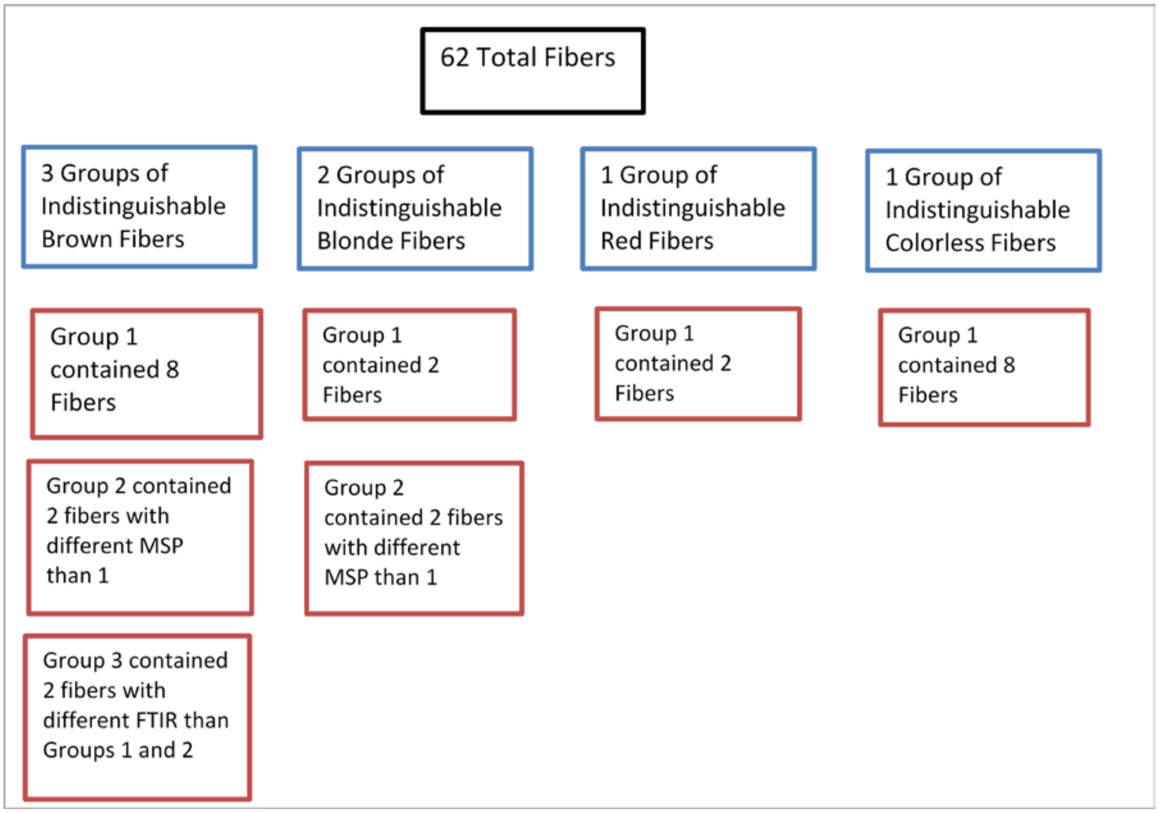


Figure 8 Data evaluation after full analytical scheme

Within the brown category, which included both 'black' and 'brown' samples, group 1 represented eight indistinguishable fibers (samples 11A, 15B, 19A, 20A, 22C, 23A, 24A and 26B) due to the presence of fish eyes, horseshoe cross-sections, and similar infrared (PAN/VC with solvent) and visible spectroscopy data. The MSP data for Group 1 brown fibers is represented in Figure 9. Group 2 represented two indistinguishable fibers, samples 22A and 31A, with similar microscopic characteristics, horseshoe cross-sectional shapes, infrared spectra (PAN/VC with solvent) and visible spectroscopy data. Group 2 differs from Group 1 in absorbance features in the visible spectrum. Group 2 fibers had minimal peak shape and absorbance curves (Figure 10) compared to Group 1. The fibers in Group 3, samples 26A and 13, were similar to each other with fish eyes, horseshoe cross-sections, similar infrared spectra (PAN/VC) and visible spectroscopy data, but were different from groups 1 and 2 in infrared data. Figure 11 represents the MSP data for Group 3.

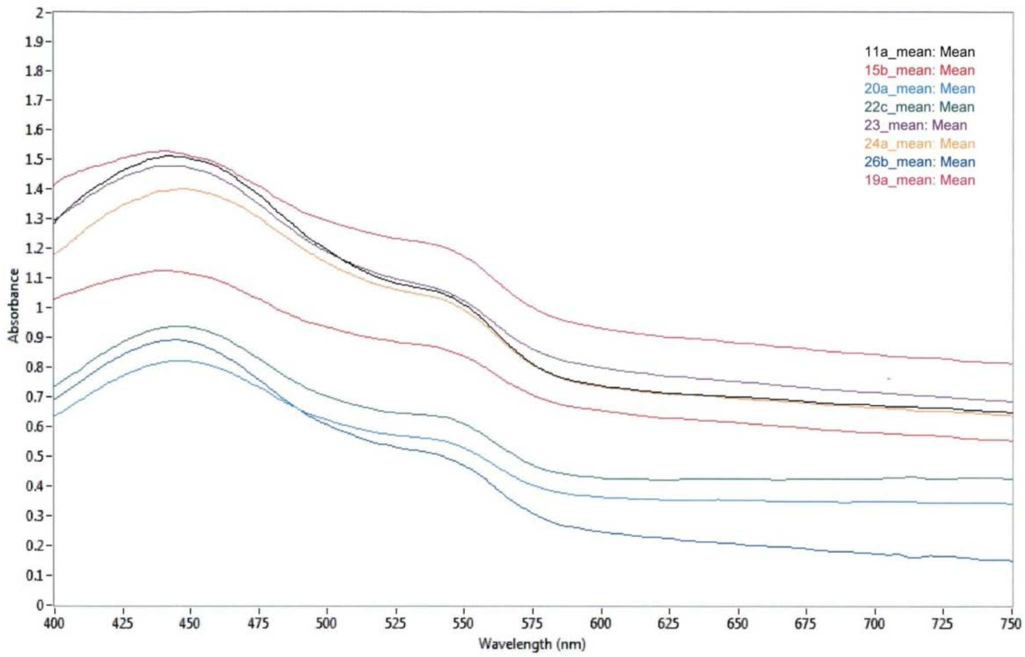


Figure 9 Mean spectra of 8 brown fibers – Group 1

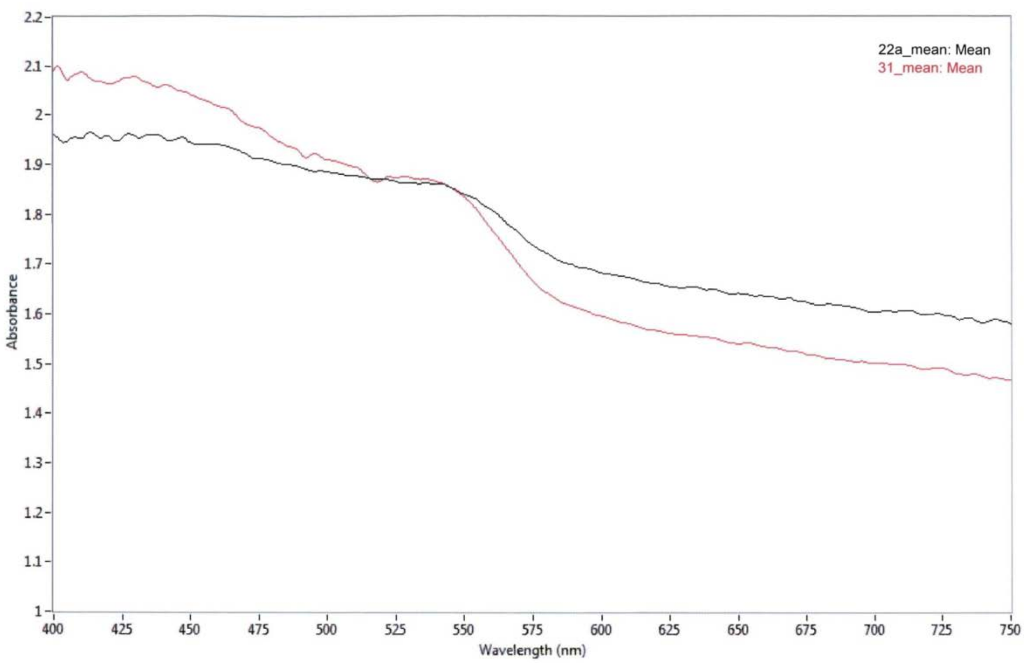


Figure 10 Mean spectra of 2 brown fibers – Group 2

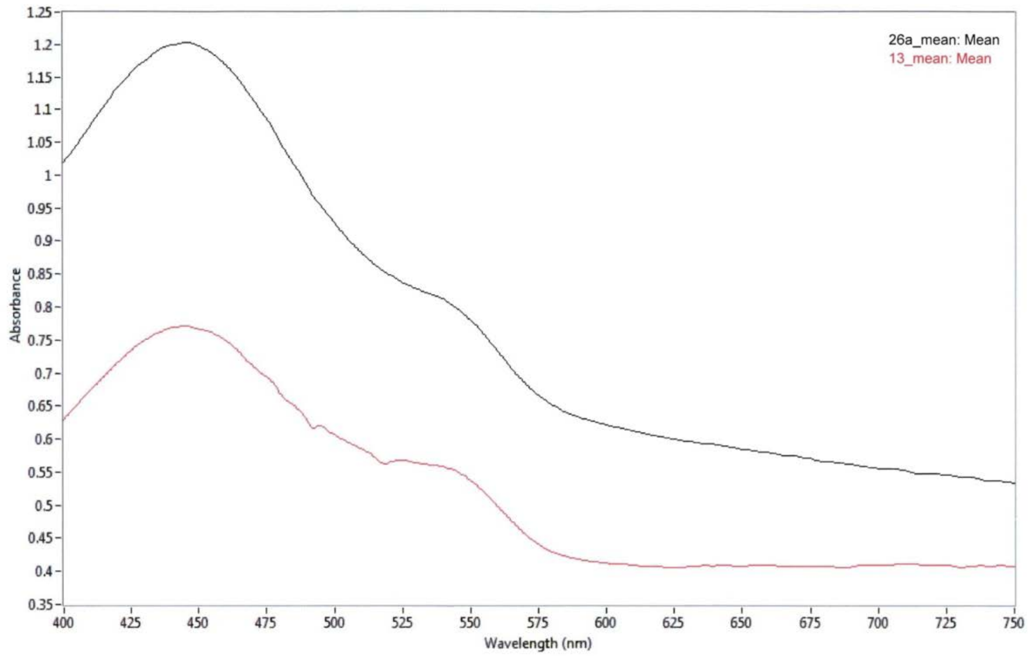


Figure 11 Mean spectra of 2 brown fibers - Group 3

The blonde category contained two indistinguishable groups. Both groups included PAN/VC fibers with fish eyes and horseshoe cross-sections but the Group 1 fibers (samples 20B and 25A) were distinguishable from the Group 2 fibers (samples 14B and 19B) by their absorbance features in the visible range. The MSP data for these blonde fibers is represented in Figure 12.

The red category contained two indistinguishable fibers, samples 18 and 19C, with fish eyes, horseshoe cross-sections, similar infrared spectra (PAN/VC) and similar visible spectroscopy (Figure 13). Eight indistinguishable colorless fibers with fish eyes, horseshoe cross-sections, and PAN/VC chemical composition remained.

Although the sample set in this study was small, variation did exist among the samples. The observable features documented did provide discrimination among fibers and infrared and MSP analysis provided further discrimination. Discrimination among the samples could have increased if additional techniques were used such as comparative microscopy and fluorescence.

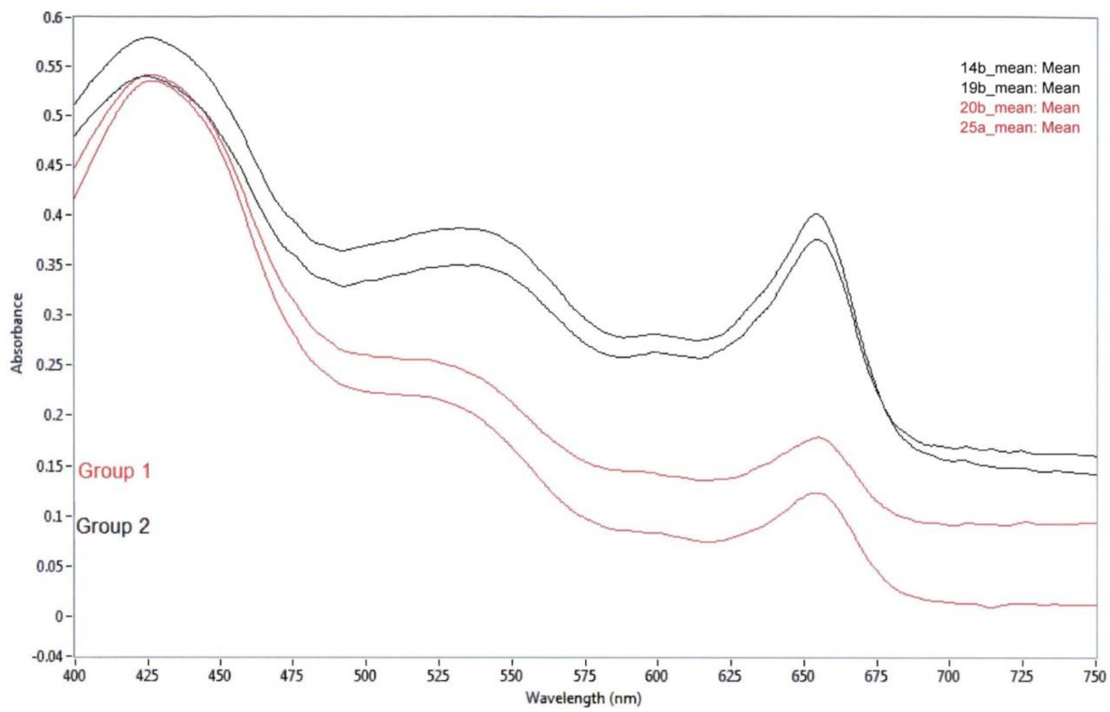


Figure 12 Mean spectra of blonde fibers

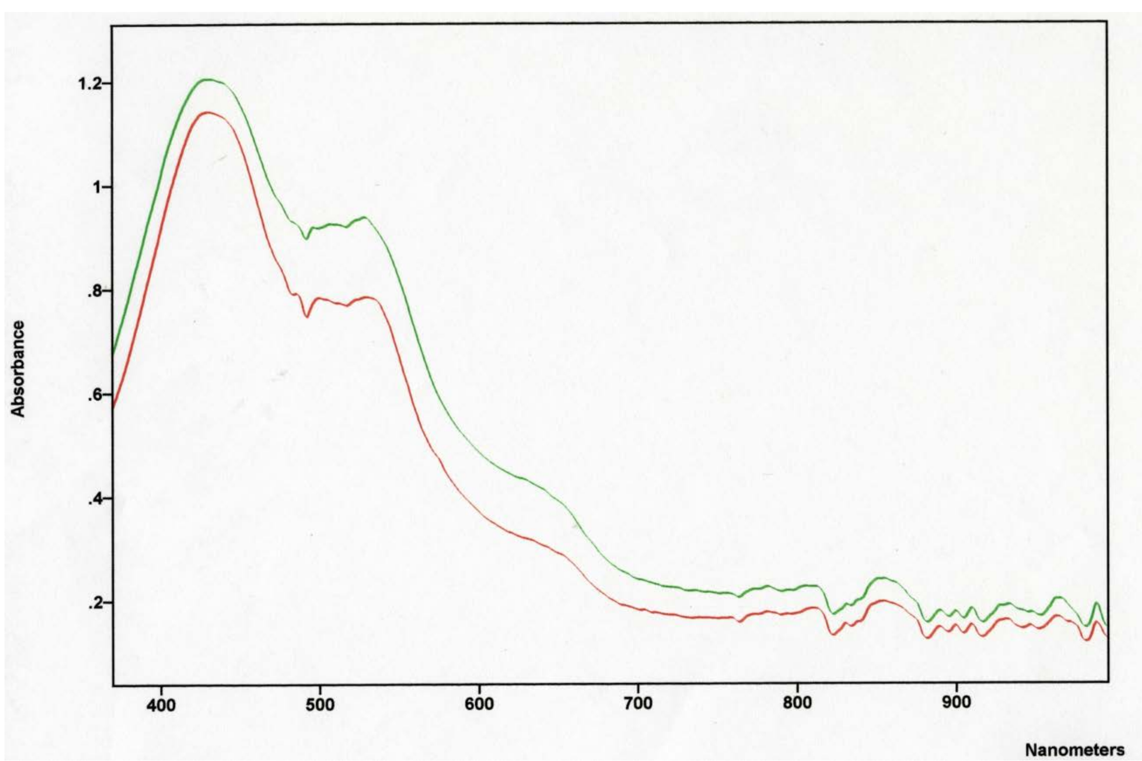
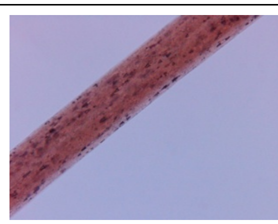


Figure 13 Mean spectra of 2 red fibers - Group 1

Intra-wig Variation

There were some interesting findings in the data relating to intra-wig variation. The sample 22 wig, manufactured by Hair U Wear under the brand name Gabor, contained three different fibers grouped into the brown category based on initial macroscopic observation (Table 3). Two of the fibers, samples 22A and 22C, were similar (based on the PLM worksheet microscopic features, cross-sectional shape and chemical composition) but differed in visible spectra (Figures 14-16) which would be expected based on the photographs below. The third fiber, sample 22B, was different in all aspects (Table 3).

Table 3. Intra variation in sample 22

Sample	**Color**	**Fish Eyes**	**Photomicrograph**	**Cross Section**	**IR Data**
22A	Brown	Yes	 100X	Horseshoe	PAN/VC with solvent
22B	Brown	No	 200X	Lobular-6 Lobes	Vinyon
22C	Brown	Yes	 200X	Horseshoe	PAN/VC with solvent

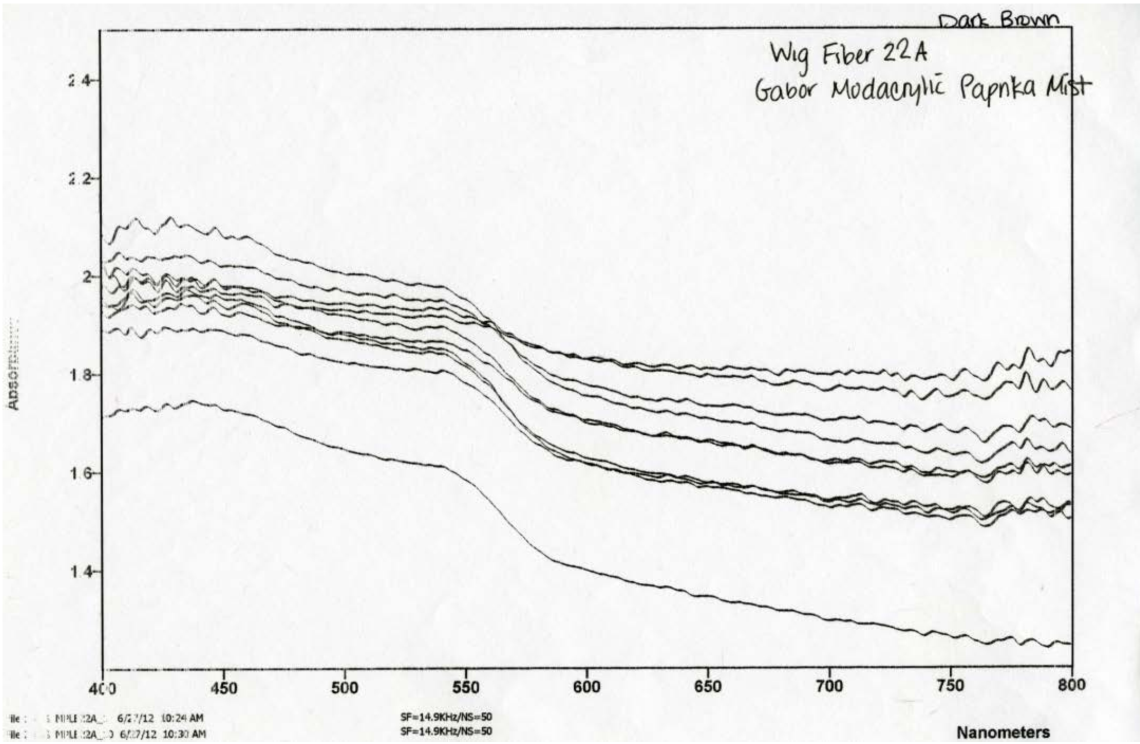


Figure 14 Sample 22A

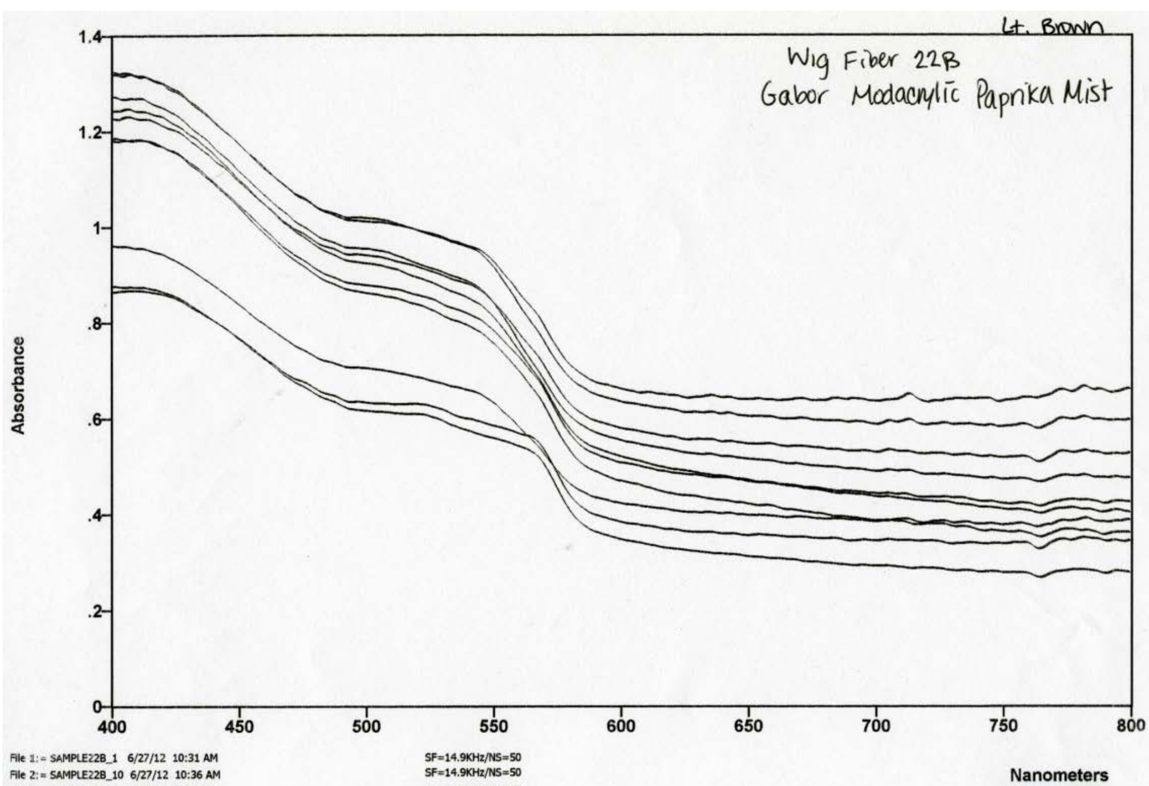


Figure 15 Sample 22B

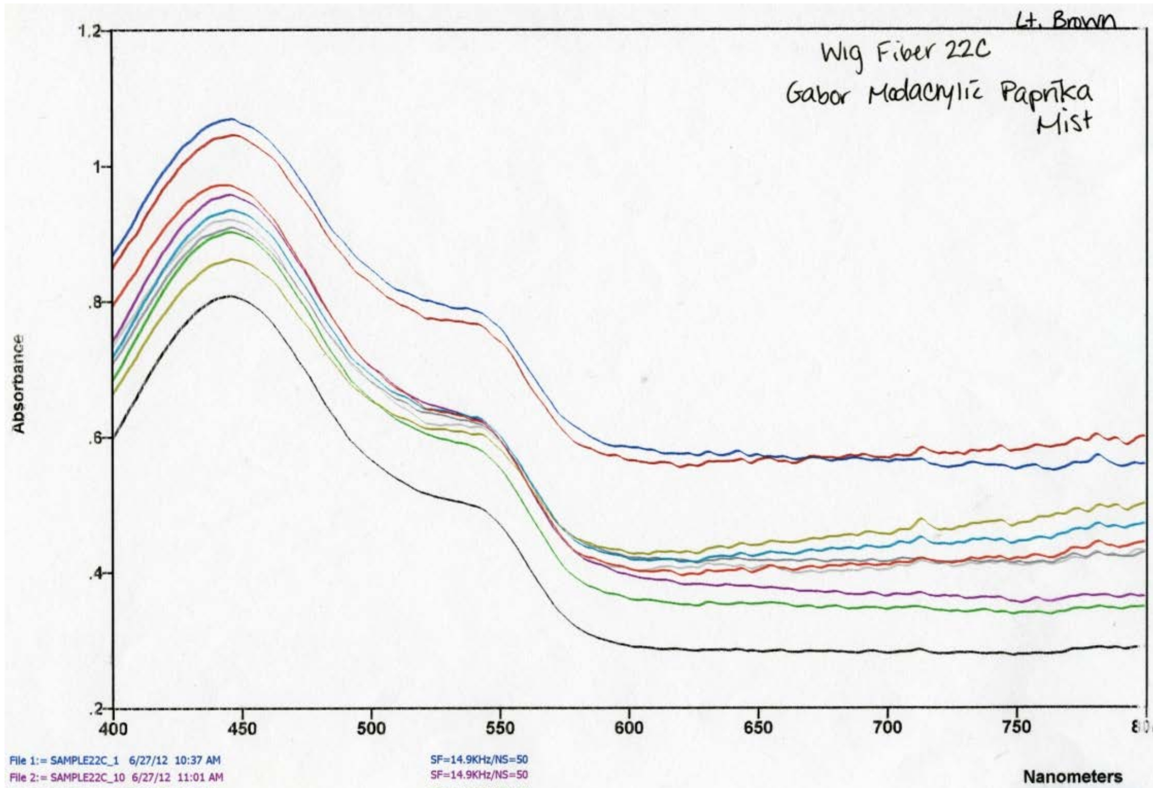


Figure 16 Sample 22C

Intra-wig variation was also found within Sample 11. Sample 11, manufactured by Revlon under the brand name Simply Beautiful, contained two fibers that were different in macroscopic color (brown and red) as well as microscopic features (absence vs. presence of fish eyes), cross-sectional shape (horseshoe vs. plumped dogbone/bean), etc. The findings of this study as a whole highlight the importance of obtaining a large representative sample of known fibers (if not the whole wig) for comparison with questioned samples as inter- and intra-wig variation may be present.

CONCLUSIONS

For those examiners with little or no training in hairs and/or fibers, the recognition of fish eyes, scale casts and/or cross-sections are all useful, yet simple techniques for determining whether a suspected hair is actually a fiber. If characteristics such as fish eyes, the absence of scales, and irregular cross-sections are observed, an examiner not trained in fiber examinations will know to forward the fiber to a fiber examiner for continued analysis which may include techniques such as FTIR and MSP. The discrimination power of the analytical scheme utilized during this study was effective when applied to the wig fiber sample set and should be a continued analytical scheme used by fiber examiners. Inter- and intra- variation in wig fiber samples should be considered during casework comparisons.

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Standard Guide for Using Pyrolysis Gas Chromatography and Pyrolysis Gas Chromatography-Mass Spectrometry in Forensic Paint Examinations

Scientific Working Group on Materials Analysis (SWGMAT)

Introduction

Various analytical techniques are available for the forensic analysis of paint. The evidentiary samples typically received by forensic laboratories may be relatively small and therefore require techniques that can provide the most information with as little sample consumption as possible. Although destructive in nature, pyrolysis gas-chromatography (Py-GC) and pyrolysis gas-chromatography/mass spectrometry (Py-GC/MS) can provide a large amount of organic chemical information from such samples. This information can be used to augment that obtained from other analytical techniques such as Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDS).

1.0 SCOPE

1.1 This document serves as a guide to assist individuals and laboratories in the utilization of Py-GC and Py-GC/MS in the forensic examination of paint. It will address the selection, application and evaluation of Py-GC and Py-GC/MS as methods for the identification and comparison of the organic components of paints.

1.2 This guideline does not purport to address any safety concerns associated with its use. It is the responsibility of the user of this document to establish appropriate health and safety practices and to determine the applicability of regulatory limitations prior to use.

2.0 REFERENCED DOCUMENTS

2.1 ASTM International Standards

- D16-11 Terminology for Paint Related Coatings, Materials and Applications
- E 1459-92(2005) Standard Guide for Physical Evidence Labeling and Related Documentation
- E 1492-11 Standard Practice for Receiving, Documenting, Storing and Retrieving Evidence in a Forensic Science Laboratory
- E1610-02(2008) Standard Guide for Forensic Paint Analysis and Comparison

2.2 Scientific Working Group for Materials Analysis

- SWGMAT Trace Evidence Quality Assurance Guidelines (January 2000). Available: www.swgmat.org/Trace%20Evidence%20Quality.pdf
- SWGMAT Trace Recovery Guidelines (October 1999). Available: www.swgmat.org/Trace%20Evidence%20Recovery%20Guidelines.pdf
- SWGMAT Forensic Paint Analysis and Comparison Guidelines. Available: www.swgmat.org/Forensic%20Paint%20Analysis%20and%20Comparison%20Guidelines.pdf

3.0 TERMINOLOGY

CAPILLARY COLUMN A long, narrow, wall coated, open tubular column used for capillary gas chromatography.

CARRIER GAS Mobile gas phase that flows through the column carrying the analyte.

CLASSIFICATION Separating samples into groups based on their properties or characteristics.

CHROMATOGRAM A presentation of data from a chromatographic system represented as a plot of the detector signal intensity vs. time.

CURIE POINT The temperature at which a ferromagnetic metal loses its ferromagnetic properties.

FLAME IONIZATION DETECTOR (FID) A detector that measures the concentration of organic species in a gas stream.

GAS CHROMATOGRAPHY (GC) An analytical separation technique that uses a gas (mobile phase) such as helium, nitrogen, or hydrogen to carry a mixture of analytes through a column that is either packed or coated with a stationary medium (stationary phase). In this technique separation occurs through differential interaction of analytes with the stationary phase.

GAS FLOW RATE The rate at which the carrier gas flows through the column.

GC TEMPERATURE PROGRAM An operator specified program that changes the temperature of the column oven over an analytical run through a computer interface.

INTERFACE TEMPERATURE The temperature of the heated zone between the pyrolysis unit and the GC.

MASS SPECTROMETRY (MS) An analytical technique that measures the mass-to-charge ratio (m/z) of gaseous ions.

MOBILE PHASE The carrier gas in a gas chromatographic system, which is inert to the sample (and moves through the chromatographic column, transporting the sample from inlet to the detector outlet).

MONOMER A repeating structural unit within a polymer.

PEAK RESOLUTION The ability to separate peaks.

POLYMER A high molecular weight compound consisting of one or more types of repeating units (monomers); it can be natural or synthetic.

PYROGRAM A chromatogram obtained from the pyrolysis products of a material.

PYROLYSIS The thermal fragmentation of a substance in an inert atmosphere.

PYROLYSIS TEMPERATURE The temperature at which the pyrolysis of the sample is performed. It can be a set temperature or a ramped temperature program depending upon the pyrolysis system.

PYROLYZATE The product of the pyrolysis process.

RETENTION TIME The time required for the elution of a component in a chromatographic system.

SPLIT RATIO The distribution of the carrier gas and injected sample between waste and the column.

STATIONARY PHASE The coating of the walls of a fused silica column. It is the phase that does not move in a chromatographic system.

TEMPERATURE PROGRAM The program set up through a computer interface by the operator controlling the temperature of the chromatographic oven.

TOTAL ION CHROMATOGRAM (TIC) The resulting display of the separated mixture after the mass spectrometer detects and identifies the components of the mixture.

TRACEABLE REFERENCE STANDARD A sample acquired or prepared with documented origin that has known properties for the purpose of calibrating equipment and/or for use as a control.

TRANSFER LINE The connection between the pyrolysis unit and the GC injection port, as well as between the GC and the MS.

4.0 SUMMARY OF PRACTICE

4.1 This guide outlines the application of qualitative and semi-quantitative Py-GC and Py-GC/MS in forensic paint analysis as described in E1610. It describes the pyrolysis of small samples, interpretation and comparison of pyrograms, and identification of the binder systems in paint. The analytical system consists of at least two distinct components: 1) the pyrolysis unit where sample pyrolysis occurs, and 2) the gas chromatograph where separation and detection of the pyrolyzate components occur. In instances where a mass spectrometer is utilized as a detector, it can be considered as a third distinct part of the analytical system. The use of a mass spectrometer assists in the identification of selected pyrolyzates.

4.2 Paint samples are complex mixtures of organic and inorganic components. Pyrolysis techniques are suitable for the analysis of the organic content. It should be noted that the inorganic content of the samples will remain behind in the sample holder after pyrolysis.

4.3 The primary organic constituent of any paint is the binder or resin. In addition to the binder, various other organic components may be present, including but not limited to pigments, plasticizers, and various additives, all of which may appear in the pyrogram and may have comparative value. As these techniques are destructive the amount of sample available must be taken into consideration. Analysis of individual paint layers is encouraged whenever practicable.

4.4 BASIC PRINCIPLES

4.4.1 Pyrolysis is the thermal fragmentation of a substance in an inert atmosphere. This process reduces larger molecules into smaller molecules through the breaking of bonds via the application of thermal energy. Analytical pyrolysis provides chemical information on various materials and enables the analysis of materials that cannot otherwise be introduced into a chromatographic system in liquid form. By operating in an inert atmosphere and strictly controlling temperature and the time of heating, macromolecular materials can be reduced to smaller molecules in a reproducible fashion. When analyzed using a separation technique such as gas chromatography, the smaller molecules produced through the action of pyrolysis will form a pattern of separated fragments carrying information about the original molecule. This procedure makes it possible to obtain structural information about high molecular weight compounds.

4.4.2 There are three primary mechanisms by which fragmentation can occur: 1) random scission, 2) monomer reversion, and 3) side group scission.

4.4.2.1 Random scission is a free radical mechanism that results in random breaks in a polymer chain. The breaks typically occur between carbon-carbon bonds on the polymer chain that have similar bond strengths. The resulting fragments have a terminal unsaturation and a range of lengths. A good example of a pyrogram produced through random scission is that of polyethylene.

4.4.2.2 Monomer reversion involves the unzipping of a polymer chain into its constituent monomers. This occurs when the bonds between monomers are the weakest links in the polymer chain. A good example of monomer reversion can be found in the pyrogram of polystyrene where the largest peak is styrene.

4.4.2.3 Side group scission occurs when side groups on a polymer chain in close proximity to one another form stable bonds with one another and are released from the polymer chain. The resulting products typically contain unsaturated bonds and may form aromatic products as in the case of polyvinyl chloride (PVC).

4.4.3 It should be noted that polymer compositions can be very complex and a combination of the above listed mechanisms commonly occur during the pyrolysis process. Examples and a thorough discussion of these mechanisms can be found in Wampler (2007).

4.4.4 The pyrograms that are produced from different polymer compositions form characteristic patterns that can be used for both identification of polymer type and comparisons between known and unknown samples.

4.5 INSTRUMENTATION

4.5.1 Pyrolysis Systems

4.5.1.1 Three different types of instrumentation are available for performing analytical pyrolysis: 1) resistively heated pyrolyzers, 2) Curie point pyrolyzers and 3) furnace pyrolyzers, all of which have advantages and disadvantages.

4.5.1.2 The most common form of pyrolysis used in the forensic laboratory is resistively heated pyrolysis. In this technique, the sample is placed either on a ribbon filament or in a quartz tube or boat that is inserted into a coiled filament. When a current is passed through the filament, resistance of the metal results in rapid heating. Transfer of heat from the filament results in pyrolysis of the sample. Temperature ramping is possible with this technique and the desired temperature can be selected by simply controlling the current. It should be noted that the coil set temperature and the amount of heat that actually reaches the sample may differ.

4.5.1.3 With inductively heated or Curie point pyrolysis, the sample is either coated on or placed in a ferromagnetic wire or foil. A radio frequency (Rf) electric current is introduced into a coil surrounding the wire or foil sample retainer. As the current passes through the coil, an electromagnetic field is generated causing the wire or foil to rapidly reach a maximum temperature (Curie point temperature) that pyrolyzes the sample. The type of wire or foil that is used will determine the maximum temperature that will be reached. This type of analysis results in temperatures that can be strictly controlled in a highly reproducible fashion. Different alloy compositions are available for a wide range of temperatures. Temperature ramping is not an option with this technique.

4.5.1.4 Furnace pyrolyzers use a quartz crucible to introduce the sample into the heated analytical chamber (furnace). The furnace is typically run isothermally (held at a single temperature). Furnace pyrolyzers are relatively inexpensive and easy to use. However, there is usually a large reaction space that can result in secondary fragmentation taking place and the relatively long equilibration times preclude the use of temperature ramping.

4.5.2 Gas Chromatography

4.5.2.1 The typical gas chromatograph contains an inlet for sample introduction, a temperature controlled oven, an analytical column(s), and a detector(s). Some systems also include a pyrolysis interface.

4.5.2.2 The inlet conditions must be suitable for the samples that are being introduced into the instrument. The inlet temperature must be high enough to prevent condensation of most pyrolysis fragments but not so high that secondary reactions and column degradation occur. The inlet temperature should not exceed the highest temperature of the oven in order to reduce the possibility of sample carryover. Typical inlet temperatures range from 200 to 300°C. The split ratio should be suitable for the sample sizes that are being analyzed. In general, the split ratio should be set so that the column and detector are not saturated by sample. A poorly chosen split ratio can result in poor chromatographic separations and saturated peaks in the chromatogram. Typical split ratios range from 20:1 to 100:1.

4.5.2.3 The choice of oven parameters is critical for the separation of pyrolyzates. Due to the wide range of fragment size that may be encountered, temperature ramps are utilized. When selecting oven parameters, several variables must be taken into consideration including the molecular weight range of fragments, the resolution required between peaks, the potential for sample carryover, and the overall run time.

4.5.2.4 The choice of column is dependent upon the polarities of pyrolyzates that are being considered. Numerous column lengths, bore diameters, and stationary phase combinations are available. A variety of column polarities can be used for Py-GC applications.

4.5.2.5 Due to the variety of polarities of pyrolyzates generated from a paint sample, the following should be considered during column selection. A high polarity column provides good resolution for isocyanates and acids formed during pyrolysis. However, they are subject to lengthy run times (approximately 45 minutes) and permanent retention of very high polarity pyrolyzates such as phthalic anhydride. A low polarity column provides adequate resolution for many paint pyrolyzates including phthalic anhydride; however, it provides poor resolution for high polarity and small sized pyrolyzates as well as acids formed during pyrolysis. A medium polarity column can be used as a compromise; however it is also subject to long run times.

4.5.2.6 The most commonly used columns for general Py-GC applications are polydimethylsiloxane-based capillary columns of at least 15 meters in length.

4.5.2.7 Various detectors are available for use with gas chromatographic systems. Some detectors have very specific uses and will not be discussed here. The two most common detectors for use with Py-GC include the flame ionization detector (FID) and mass spectrometer (MS).

4.5.2.8 The flame ionization detector is capable of detecting a broad range of combustible pyrolyzates. It is relatively inexpensive, has a large linear dynamic range, and can therefore handle a wide range of sample sizes. In this respect it is not easily susceptible to being overloaded with sample. These attributes make it a common detector for gas chromatographs. Identifications and comparisons with data from an FID are based on retention times of peaks and the appearance of overall pyrogram patterns. Significance of comparisons and identifications with this type of detection can be enhanced when two columns of differing polarities are used simultaneously (Saferstein and Ostberg).

4.5.2.9 Various types of mass spectrometers are available for use as GC detectors. The choice of mass spectrometer is dependent upon various factors including cost and type of analysis being performed. A discussion of the various types of mass spectrometers is beyond the scope of this document.

4.5.2.10 Several different types of ionization sources are available for use. Of the two most common sources in forensic laboratories, chemical ionization and electron ionization, the latter tends to be more useful for the applications discussed in this guide. The mass spectra that are produced often contain a large amount of structural information that can aid in identifying the pyrolysis products.

4.5.2.11 Mass spectral analysis can also be used to extract specific information from the data. By selecting ions of interest, classes of compounds can be selectively viewed and searches for specific compounds are possible.

5.0 SIGNIFICANCE AND USE

5.1 Pyrograms generated from Py-GC can be used to compare questioned and known paint samples and to identify major constituents. Classification entails analyzing reference standards and empirically assigning peaks in the pyrogram.

5.1.1 The pyrolysis process breaks macromolecular structures into smaller, more volatile units and releases smaller compounds from the complex binder matrix.

5.1.2 The gas chromatograph serves as a method for the separation and detection of the fragments and compounds formed/released during the pyrolysis process.

5.1.3 The mass spectrometer has the potential for identification of paint components. It should be noted that the pyrolyzates produced are not necessarily the same materials that were originally added in the manufacturing process prior to polymerization. The mass spectrometer also has the ability to resolve co-eluting components and provide mass fragmentation patterns for both compounds.

5.1.4 The reconstructed total ion chromatogram looks similar to and provides the same information as a pyrogram from conventional Py-GC analysis. However, it also often provides confirmation of peak identities that can aid in classification of the type of polymer (e.g., acrylic or epoxy) or additive and permit identification of the chemical differences between differing compositions (methyl methacrylate vs. butyl acrylate). Considering the complexity of a pyrogram, this additional information should not be construed as an improvement in discrimination power.

5.1.5 Narrow bore capillary columns used in Py-GC typically require higher injection port split ratios to avoid over-loading of the column. These higher split ratios result in reduced detection of minor pyrolyzates, which in turn reduces the amount of thermal fragmentation information acquired from the pyrolysis process. Py-GC systems using flame ionization detectors can employ medium bore capillary columns that can sustain much higher sample loading. This may permit the use of smaller sample sizes and/or the detection of minor pyrolyzates, often having peak areas less than 0.1 percent of the total pyrolyzate. It should be noted that if a medium bore column is used, a decrease in resolution should be expected.

5.1.6 The use of two independent chromatographic columns (one high polarity and one low polarity) in Py-GC systems may provide improved resolution and discrimination over that obtained from a single column. (Saferstein & Ostberg and Ryland, Jergovich, Kirkbride).

6.0 SAMPLE HANDLING

The general collection, handling and tracking of samples shall meet or exceed the requirements of ASTM E 1492-11 as well as the relevant portions of SWGMAT's Trace Evidence Quality Assurance Guidelines Document.

6.1 Sample preparation

6.1.1 Prior to sampling, efforts should be made to scrape away or otherwise remove any foreign debris or contaminants that are visually observed by stereomicroscopy.

6.1.2 For multi-layer paints, the recommended method is to physically separate all layers of the paint for analysis via Py-GC or Py-GC/MS. This method allows the binder from each layer to be effectively characterized.

6.1.2.1 Many forensic paint samples are too small in size to isolate individual paint layers and also provide for replicate analysis. When sample size is limited, it is advisable to prepare replicate samples of intact chips of multi-layered paint systems. Care should be taken to ensure that a similar layer system is prepared for both the known and questioned paints.

6.1.3 The sample size required may vary according to sample type, pyrolysis method, column type used, chromatographic conditions and detection method. Typically, sample size should be in the range of 5-100 micrograms. Samples analyzed in replicate and for comparison purposes should be similar in shape and size.

7.0 ANALYSIS

Pyrolysis involves the thermal degradation of the sample in an inert atmosphere resulting in the breaking apart of the polymer system into monomers and other pyrolysis products. The instrument operating conditions should be optimized for pyrolysis (e.g., time and temperature), chromatographic separation (e.g., column selection, temperature programming), and detection.

7.1 Pyrolysis Temperature

7.1.1 The pyrolysis unit must pyrolyze the sample at a set temperature and at a reproducible heating rate for a specific duration to ensure reproducibility of the polymer fragmentation.

7.1.2 The pyrolysis temperature must allow for complete pyrolysis without causing excessive bond breakage. Excessive fragmentation will render the resulting pyrogram very difficult to interpret and may destroy discriminating higher molecular weight pyrolyzates. A method for checking for complete pyrolysis might include re-running the system at a higher temperature with the original sample in place after the initial run has been completed. If peaks are observed, pyrolysis was not complete and a higher temperature should be used. Repeat this process until complete pyrolysis is attained.

7.2 Gas Chromatograph Parameters

7.2.1 The gas chromatograph must have a reproducible temperature profile and a stable carrier gas flow rate.

7.2.2 Oven temperature, ramp rates, column type, and gas-flow rates influence the pyrograms obtained. The conditions should be chosen based on the quality of pyrograms produced with regard to peak separation, resolution and reproducibility. Examples of instrumental conditions can be found in a variety of references (Burns and Doolan, Challinor 2001, Plage, et. al., Ryland et. al., Saferestein and Ostberg 1988, Wampler 1997 and 2007, and Wright, et. al.).

7.3 Mass Spectral Range

A scan range should be chosen in order to allow analysis of large molecular weight fragments, while disregarding lower molecular weight fragments that may unnecessarily clutter the mass spectrum.

7.4 Quality control

Quality control procedures should be established and documented by the laboratory.

7.4.1 Sample Containers

7.4.1.1 If a sample container is re-used (e.g. quartz tube, crucible, or metallic foil), it must be cleaned before each use. Each laboratory should develop, document and use a cleaning procedure that demonstrates the container is free of contamination on subsequent runs. One method for cleaning sample containers includes firing them in an apparatus prior to use. A blank run can be performed using a clean container to ensure that no pyrolyzable residues are present.

7.4.1.2 Containers should be discarded if they are damaged or significant residues have built up.

7.4.1.3 When using a platinum coil pyrolysis probe, care must be taken to ensure even spacing of the coils. In addition, the position of the sample inside the sample container should be the same for all samples to ensure reproducibility. In the case of quartz tubes, samples may be retained in position in the tube by the addition of quartz wool or a filler post.

7.4.2 Blanks

7.4.2.1 A system blank must be run prior to analyzing any case samples to ensure that there is no contamination and/or carryover. The system blank should include all aspects of the system.

7.4.2.2 A system blank should also be run in between samples in order to demonstrate that carryover is not occurring.

7.4.2.3 Acceptable maximum peak heights in blank runs should be defined in laboratory procedures.

7.4.3 Performance Check

Prior to use, the performance of the instrument must be verified.

7.4.3.1 Instrument verification may be done by analyzing a sample of a standard polymer such as polyethylene, polystyrene, or Kraton 1107.

7.4.3.2 The pyrogram produced by the standard should meet the laboratory's established quality control criteria.

7.4.3.3 For Py-GC/MS, the mass spectrometer must be tuned using a standard reference compound to ensure optimization of peak shape, accurate mass assignments, and sensitivity.

7.4.4 Maintenance and troubleshooting

7.4.4.1 Scheduled routine maintenance procedures are recommended to ensure proper operation of the instrument. They should be performed per individual laboratory procedures. These may include cleaning the detector, reassembling the detector and checking flows, changing GC septa and pyrolysis probe seals, cleaning the injection port, checking/changing glass liners, and performing other cleaning as needed.

7.4.4.2 Maintenance and troubleshooting procedures should be suitably documented. The instrument performance should be checked after maintenance is carried out (e.g., column change or instrument configuration change).

8.0 INTERPRETATION

8.1 Classification/Identification of Paint Components

This document does not purport to set a standard for the identification of individual pyrolyzates. Analysts may find it appropriate to identify certain pyrolyzates or patterns of pyrolyzates in order to classify the binder type or sub-type. The confidence with which such identifications are made will vary depending upon the system used (e.g., single column, two distinct columns, mass spectrometry).

8.1.1 Identifications of compounds can be accomplished by comparison to known samples or to a mass spectral library. Reference chromatograms should originate from the same instrument and protocol used in the current analysis. The reference standards used in creating libraries should be traceable.

8.1.2 Single component additives (e.g., plasticizers) can often be identified via mass spectral library searches. It is important to note that many of these components are the result of thermal desorption instead of pyrolysis.

8.2 Comparison

8.2.1 Pyrograms can be compared side-by-side or using overlays. There are a number of significant factors that should be considered when comparing pyrograms including retention time, shape, relative intensity, or presence/absence of peaks. It may be necessary to assess heterogeneity through the analysis of replicate samples.

8.2.2 The presence of additional peaks could be inherent differences between the samples or from extraneous material adhering to the sample. If extraneous material is suspected as the source of the difference, the original sample should be cleaned and additional samples prepared for pyrolysis.

8.2.3 For pyrograms to be considered indistinguishable, the retention time of the peaks should have reasonable agreement with each other. In general the positions of corresponding peaks in two or more pyrograms being compared should be within a certain time frame of each other (e.g., ±0.1 minute, 2%). For sharp peaks, one may use tighter constraints and with broad peaks, greater variation may be acceptable.

8.2.4 For pyrograms to be considered indistinguishable, the shape of the peaks should be consistent between comparison samples. The peak width and symmetry should be evaluated. Sample size may affect the peak width and resolution.

8.2.5 For pyrograms to be considered indistinguishable, the relative intensities of the respective peaks should be similar between comparison samples. The relative intensity may be affected by the heterogeneity of the sample, sampling, size of sample, or reproducibility of the pyrolysis process.

8.3 Conclusions

Three conclusions can be reached after evaluating and comparing the known and questioned pyrograms: 1) the pyrograms are dissimilar, 2) the pyrograms are indistinguishable, or 3) inconclusive.

8.3.1 The pyrograms are dissimilar if there are one or more significant differences in the pyrograms. Significant differences are differences in which the variation between pyrograms cannot be explained other than as differences between samples.

8.3.2 The pyrograms are indistinguishable if there are no significant differences in the pyrograms. Differences are not significant if the variation can be explained as something other than differences between samples.

8.3.3 An inconclusive determination is one in which constraints of sample size or condition precludes a decision as to whether differences are significant or not.

9.0 DOCUMENTATION

9.1 When making comparisons of paint, similarity or dissimilarity in the pyrograms should be noted.

9.2 Case notes should include a copy of all of the instrumental data that was used to reach a conclusion. All copies should include a unique sample designation, the operator’s name/initials, and the date of analysis.

9.3 Case notes should also include a description of the evidence analyzed, the method of sample preparation employed, and the analytical instrumentation used with the operating parameters.

9.3.1 The following variables should be included:

Pyrolysis Conditions

- Pyrolysis unit
- Interface/Standby temperature
- Pyrolysis temperature and time
- Ramp rate (if used)

Gas Chromatography Conditions

- Instrument used
- Column used (including length, diameter, coating, coating thickness)
- Injection port temperature
- Carrier gas and flow rate
- Inlet pressure
- Split Ratio
- Oven temperature (including initial-final temperatures, ramp rates, durations)
- Detector type
- Detector Conditions
- Interface (transfer line) temperature

9.4 See SWGMAT's Trace Evidence Quality Assurance Guidelines and Expert Reporting Guideline for further requirements.

10.0 REFERENCES

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Guideline for Assessing Physical Characteristics in Forensic Tape Examinations

Scientific Working Group for Materials Analysis (SWGMAT)

1.0 Scope

This document is part of a series of SWGMAT guidelines relating to the forensic analysis of tape and is intended to assist individuals and laboratories that conduct physical examinations and comparisons of pressure sensitive tapes. Its aim is to provide a description of the methods used to assess the physical characteristics of tape evidence.

2.0 Reference Documents

ASTM International Standards

- D1535 *Standard Practice for Specifying Color by the Munsell System*
- E308 *Standard Practice for Computing the Colors of Objects by using the CIE System*
- E1459 *Standard Guide for Physical Evidence Labeling and Related Documentation*
- E1492 *Standard Practice for Receiving, Documenting, Storing, and Retrieving Evidence in a Forensic Science Laboratory*

SWGMAT Trace Evidence Quality Assurance Guidelines (January 1999). Available: http://swgmat.org/Trace%20Evidence%20Quality.pdf

SWGMAT Trace Recovery Guidelines (January 1998). Available: http://swgmat.org/Trace%20Evidence%20Recovery%20Guidelines.pdf

SWGMAT Forensic Fiber Documents. Available: http://swgmat.org/fiber.htm

SWGMAT Guideline for the Forensic Examination of Pressure-Sensitive Tapes (August 2007). Available: http://swgmat.org/Pressure%20Sensitive%20Tape%20guideline.pdf

3.0 Terminology

Adhesive: A material that will hold two or more objects together solely by intimate surface contact

Backing: A thin flexible material to which the adhesive is applied

Calendering: The use of a multi-roll device that uses heat and pressure to apply adhesive to a tape backing

Duct tape: Fabric-reinforced tape used for general utility applications

Electrical tape: Polyvinyl chloride (PVC)-backed tape with specific dielectric properties designed for electrical applications

Fill yarn: Yarns in the scrim fabric of reinforced tape that run crosswise, perpendicular to the warp direction; also referred to as weft yarns

Filament tape: A fiber-reinforced tape in which the reinforcing fibers are only in the warp direction; also referred to as strapping tape

Long-wave UV illumination: In the wavelength range from 400 nm – 315 nm with peak wavelength energy at 366 nm

Machine direction: The direction of the tape that runs the length of the tape

Masking tape: Paper-backed tape having a creped, usually beige or buff-colored backing. Painter's tape is a type of masking tape available in a number of colors.

Nominal width: The design width of the tape, usually in terms of round numbers. Measured width can vary slightly from nominal width.

Packaging tape: a) Pressure-sensitive tape consisting of an oriented polymer with a brown or clear adhesive layer, or b) Paper-backed tape, which has a moistenable adhesive

Physical end match: A one-of-a-kind fit between two pieces of torn or cut ends demonstrating that the two pieces were once one continuous piece.

Scrim: A loosely-woven gauze-type cloth added to duct tape for reinforcement and strength

Scrim count: The dimensional count of the scrim, in terms of yarns per inch, expressed as warp count by fill count

Short-wave UV illumination: In the wavelength range from 280 nm –100 nm with the peak wavelength energy at 254 nm

Stereomicroscope: A microscope containing two separate optical systems, one for each eye, giving a stereoscopic view of a specimen

Strapping tape: See filament tape.

Texturized yarn: Crimped reinforcement fibers designed to give bulk

Twist: The direction of twist in yarns is indicated by the capital letters S and Z. Yarn has an S-twist if when it is held vertically, the spirals around its central axis slope in the same direction as the middle portion of the letter S, and Z-twist if they slope in the same direction as the middle portion of the letter Z.

Warp yarns: Yarns in scrim fabric of reinforced tape that run lengthwise (in the machine direction)

Weft yarns: See fill yarns.

Yarn: For the purposes of this document, yarns refer to lengths of fiber reinforcement: twisted staple fibers or filament fibers.

4.0 Summary of Guideline

Tape specimens can be examined to determine a common source or possible manufacturer. This guide covers visual and stereomicroscope examinations for color, thickness, reinforcement, and backing and adhesive features. Structural details, such as design, construction, and composition, can provide information that may assist the analyst in reaching a conclusion.

A goal of a tape comparison is to assess the significance of any observed differences. If no significant physical differences are found between samples, instrumental analyses are warranted.

5.0 Significance and Use

Physical characterization of tape specimens is the initial step of a comprehensive forensic pressure sensitive tape analysis. The construction, composition, and color of tapes vary and, therefore, are useful characteristics for forensic examinations. Visual characteristics and physical measurements are the quickest, most discriminating and least invasive examinations.

6.0 Sample Handling

6.1 An effort should be made not to alter the condition of a questioned specimen before the preliminary examination. In some circumstances, it may be desirable to obtain a sample cutting from the tape before a sample is analyzed for latent fingerprints. Necessary precautions should be taken to eliminate loss or contamination of other types of evidence (e.g., latent prints, DNA, and other trace evidence).

6.2 Samples for testing should not be cut from the ends of the tape if there is a possibility of a physical end match between specimens. A sample should be obtained from an area that does not interfere with the existing end(s), and the location should be marked.

6.3 If tape is received in a tangled condition an attempt should be made to separate it manually with a careful peel. More aggressive techniques such as gentle heat, liquid nitrogen, freezing, or solvents can be used if necessary. However, these techniques could affect the outcome of subsequent analyses and should, therefore, be applied only to the extent necessary.

6.4 All procedures must be conducted in such a manner to ensure that no cross-contamination occurs. The item must be photographed or described prior to conducting any analyses in order to provide documentation of its original condition. Transient evidence (e.g., hair, fiber, paint) should be preserved and documented.

6.5 Tape may not be in its original state due to weathering, stretching, chemicals, etc. These changes may limit the information obtained from the analyses. If the tape does not allow for the full range of examinations, the examinations and analyses that are performed should be reflected in the analyst's notes, and the reasons for the limited examinations should be documented.

7.0 Analysis

Written descriptions, sketches, photography, or other imaging methods must be used to document each sample's characteristics.

A preliminary visual examination of tape construction should include its general appearance, both with the unaided eye and using a stereomicroscope.

For all pressure sensitive tapes, document and record any physical damage (e.g., worn, cut, torn, frayed). The following general visual characteristics should be observed and documented:

- General condition, including any adhering matter
- Tape core markings and packaging information, if available
- Wad, flat pieces, or fragments
- Dimensions (e.g., width and length)
- Number of pieces
- Colors

- Condition of the ends for possible physical matches

7.1 Physical end match
When conducting comparison examinations between two or more tape specimens, the free ends should be carefully examined for possible physical end matches. Even though this type of association is the most compelling type of association, the analyst may elect to continue with a complete analytical analysis of these specimens depending upon the quality of the end match.

7.1.1 General guidelines for physical end match examinations:

- Observe the tear or cut pattern from the backing and adhesive side of both specimens to determine if a physical association is plausible. To observe finer detail, a stereomicroscope should be used to examine the ends.

- If the backing is distorted or folded over and adhered to the adhesive layer, gently straighten it out to restore the torn/cut edge. This may be accomplished with the careful use of forceps, gentle heat, mild solvent, or by freezing.

- Depending on the type of tape, manufacturing marks, creping on a paper backing, printing or any other continuous surface features may be present across fractured edges and would provide additional points of comparison.

- Determine if there are individualizing characteristics (e.g., a flaw or mark) that extends across the fracture. This would be an accidental or anomalous mark that initiates on one piece and terminates across the fracture edge on the other.

- If the tape has a fabric reinforcement layer, solvent (e.g., hexane, chloroform, or xylene) may be used to remove a sufficient amount of adhesive to expose the fabric and ensure alignment of the yarns that have broken across the torn ends.

- Any physical associations must be documented with descriptive notes. Physical associations between specimens that link a suspect to a crime scene or to a victim should be imaged. The imaging method should be dimensionally accurate and include a measuring scale if possible.

- It is strongly recommended that any/all physical end match associations between a questioned specimen and a known specimen be verified by another qualified analyst.

7.2 Physical Features
Tape examinations involve a process of documenting all of the physical characteristics exhibited.

The following characteristics should be documented when applicable:

- Color of adhesive and backing
- Surface texture
- Width measurement
- Overall thickness
- Backing thickness

Each of these characteristics can have a number of sub-elements, all of which can be characterized to complete the examination. Physical characteristics of a tape may change after removal from the original roll (e.g., weathering, sample handling). The analyst must decide what is an acceptable variation based on the circumstances of the case. Any measuring devices used should be properly checked with applicable quality assurance and control procedures.

7.2.1 Backing
The type of backing must be recorded (e.g., paper, polymer film). The backing should be visually and stereomicroscopically examined for color, texture, and appearance under multiple illumination sources. For comparative examinations, a side-by-side color comparison of two or more backings is appropriate; otherwise, the Munsell or International Commission on Illumination (CIE) color systems may be utilized.

7.2.1.1 Markings on the Backing
Using a stereomicroscope the tape should be examined for features such as calendering marks, striations, dimples, and inclusions. The shapes and type of markings should be documented.

7.2.1.2 Multiple Layer Backings
Tape backings should be examined to determine if multiple layers are present. This can be accomplished by cross-sectioning the tape backing via hand-sectioning or microtoming. One hand-sectioning method is as follows:

- The backing can be removed from the tape adhesive and fabric (though this is not necessary, particularly if the adhesive layer structure is also of interest).
- Two glass slides act as a sample holder by placing the bulk of the tape backing flat between them, with a small portion of the backing remaining outside the edges of the slides.
- The glass slides with the tape backing are attached to a holder (e.g., held with office tape to the side of a 2" pillbox) and positioned under a stereomicroscope such that the slides and backing are perpendicular to the microscope platform.
- Liquid nitrogen or propellant from an aerosol duster is used to freeze that small portion of the backing to make it more rigid for cutting.
- A series of cuts are taken through the edge of the tape backing with a single-edged razor blade positioned nearly parallel to the platform and nearly perpendicular to the backing and slides. The razor blade should also be cooled along with the backing for efficient cutting. Very thin cross-sections are required for proper examination.
- The cross-section(s) are collected and examined with a compound microscope using transmitted light in order to determine layer structure.

The multiple layers should be characterized and then analyzed with appropriate analytical instrumentation.

7.2.2 Adhesive
The adhesive should be visually and stereomicroscopically examined for color and appearance under multiple illumination sources. For comparative examinations, a side-by-side color comparison of two or more adhesives is appropriate; otherwise, the Munsell or CIE color systems may be utilized. Some duct tape adhesives may be multi-layered, and cross-sections of the adhesives should be made when deemed necessary. The layer structure of the adhesive could be evaluated by examination of a cross-section of the ***intact*** tape, prepared using a method like that described in Section 7.2.1.2.

7.2.3 Reinforcement
If reinforcement, such as scrim or filament fibers, is present in a tape, it should be characterized.

7.2.3.1 Duct Tape Reinforcement

The three main features to examine in duct tape reinforcement are weave, yarn description and scrim count.

The weave of the scrim fabric should be assessed using the stereomicroscope. This may require separating the adhesive from the scrim. The most frequently encountered weave patterns are weft-insertion and plain weave. Weft-insertion has chain-stitch warp yarns with texturized filaments in the fill direction. A plain weave has a one over/one under pattern; the warp and fill directions can be a combination of any of the following types of yarns:

- twisted yarns (Z- or S-twist)
- filament fibers bound by another filament fiber
- texturized filament fibers
- straight filament fibers

The fluorescence of the yarns/fibers should be examined using short- and/or long- wavelength illumination.

The scrim count, the warp count per inch and the fill count per inch, should be measured and recorded.

7.2.3.2 Strapping (Filament) Tape Reinforcement
The fibers in filament tape most often consist of synthetic or glass fibers. The fibers are only in the warp direction. The number of bundles across the width of the tape or per unit length should be counted.

The fluorescence of the filament fibers should be examined using short- and/or long- wavelength illumination.

7.2.4 Within-roll variability of physical features
Within-roll variability in some measured physical features is possible, such as tape width, thickness, and scrim count. When variances are observed in the comparison of two tape samples in which all other features are similar, the analyst must decide on an acceptable tolerance. When available, within-roll variances are best derived from a known roll submitted with the case. Alternatively, similar products may be assessed to gain insight into expected variances. Approximate industry tolerances for these features may be found in Mehltretter 2012.

8.0 Report Documentation

The goal is to produce documentation that will be meaningful to a reviewer in the absence of the recording analyst. The resulting notes must be sufficient to support the conclusions reached in the analyst's report. All pertinent data, including any documentation of physical end matches, should be placed into or referenced within the case file. For comparative tape examinations, if significant differences are observed in physical characteristics, no further testing is necessary, and a report can be issued. If no significant differences are observed, instrumental examinations should be performed before a report is issued. Any limitations that affect the conclusions (e.g., sample size, condition of the sample) should be addressed in the report. In sourcing cases, instrumental examinations may be necessary before a report is issued.

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Standard Guide for Using Pyrolysis Gas Chromatography and Pyrolysis Gas Chromatography/Mass Spectrometry in Forensic Tape Examinations

Scientific Working Group for Materials Analysis (SWGMAT)

1.0 Scope

This document is part of a series of SWGMAT guidelines describing the forensic analysis of tape and serves as a guide to assist individuals and laboratories in the utilization of pyrolysis gas-chromatography (Py-GC) and pyrolysis gas-chromatography/mass spectrometry (Py-GC/MS) for tape analysis.

Py-GC and Py-GC/MS can provide valuable organic chemical information of tape samples. The techniques may be performed on the backings and adhesives of most tape types. The information obtained can be used to augment that obtained from other analytical techniques such as Fourier transform infrared spectroscopy (FTIR), polarized light microscopy (PLM), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), and X-ray fluorescence spectroscopy (XRF).

The purpose of this guide is to provide direction on sample preparation techniques, parameters to consider when optimizing and validating a method, and what information the data provides. This guide is not intended to be an instruction book, nor will it apply in every situation. The methods employed by each examiner and/or laboratory depend on sample size, sample suitability, and laboratory equipment. It is assumed that the examiner has a basic knowledge of the theory and requisite proficiency in the use of Py-GC and/or Py-GC/MS. Further, it is the responsibility of the analyst to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to the use of this technique.

2.0 Reference Documents

2.1 ASTM International Standards

E 1492 Standard Practice for Receiving, Documenting, Storing and Retrieving Evidence in a Forensic Science Laboratory

2.2 Scientific Working Group for Materials Analysis

SWGMAT Trace Evidence Quality Assurance Guidelines (January 1999). Available: http://swgmat.org/Trace%20Evidence%20Quality.pdf

SWGMAT Guideline for Forensic Examination of Pressure Sensitive Tapes (August 2007). Available: http://swgmat.org/Pressure%20Sensitive%20Tape%20guideline.pdf

3.0 Terminology

The terms defined relate specifically to Py-GC and Py-GC/MS analysis as described in this document. General tape definitions can be found in the SWGMAT Guideline for the Forensic Examination of Pressure Sensitive Tapes.

Capillary column: A long, narrow, wall-coated, open tubular column used for capillary gas chromatography

Carrier gas: Mobile gas phase that flows through the column carrying the analyte

Classification: Separating samples into groups based on their properties or characteristics

Chromatogram: A presentation of data from a chromatographic system represented as a plot of the intensity of the detector signal vs. time

Gas chromatography (GC): An analytical separation technique that uses a gas (mobile phase) such as helium, nitrogen or hydrogen to carry a mixture of analytes through a column that is either packed or coated with a stationary medium (stationary phase); separation occurs through differential interaction of analytes with the stationary phase

Gas flow rate: The rate at which the carrier gas flows through the column

GC temperature program: An operator-specified program that, through a computer interface, accurately changes the temperature of the column oven over an analytical run

Interface temperature: The temperature of the heated zone between the pyrolysis unit and gas chromatograph

Mass spectrometry (MS): An analytical technique that measures the mass-to-charge ratio (m/z) of gaseous ions

Monomer: A repeating structural unit within a polymer

Mobile phase: The carrier gas in a gas chromatographic system

Peak: Gaussian-shaped (ideally) instrumental response at a specific time

Peak resolution: The ability to separate peaks

Polymer: A high molecular weight compound consisting of one or more types of repeating units (monomers); can be natural or synthetic

Pyrogram: A chromatogram obtained from the pyrolysis products of a material

Pyrolysis: The thermal fragmentation of a substance in an inert atmosphere

Pyrolysis temperature: The temperature at which the pyrolysis of the sample is performed; can be a set temperature or ramped temperature program depending on the pyrolysis unit

Pyrolyzate: The product of the pyrolysis process

Retention time: The time required for the elution of a component from a chromatographic system

Split ratio: The distribution of carrier gas and injected sample between waste and the column

Stationary phase: The coating of the walls of a fused silica column; the phase that does not move in a chromatographic system

Total ion chromatogram (TIC): The resulting display of the separated mixture after the mass spectrometer detects and identifies the components of the mixture

Traceable reference standard: A sample acquired or prepared with documented origin that has known properties for the purpose of calibrating equipment and/or for use as a control

Transfer line: The connection between the pyrolysis unit and the GC injection port, as well as between the GC and MS

4.0 Summary of Practice

4.1 This guide outlines the application of Py-GC and Py-GC/MS in forensic tape analysis. It describes the pyrolysis of small samples of backings and adhesives, interpretation and comparison of pyrograms, and identification of the polymer constituents in tapes. The analytical system consists of at least two distinct components: 1) the pyrolysis unit where sample pyrolysis occurs and 2) the gas chromatograph where separation and detection of the pyrolyzate components occur. In instances where a mass spectrometer is utilized as a detector, it can be considered as a third distinct part of the analytical system. The use of a mass spectrometer assists in the identification of selected pyrolyzates.

4.2 Tape samples are complex mixtures of organic and inorganic components. Since pyrolysis techniques are suitable for the analysis of the organic content, this document will focus on the organic constituents of tapes. However, it should be noted that the inorganic content of the samples will remain behind in the sample holder after pyrolysis.

4.3 The organic constituents of any tape are the polymer, elastomer, plasticizers, tackifying resins, and/or additives. These constituents may appear in the pyrogram and have comparative value. As pyrolysis techniques are destructive, the amount of sample available must be taken into consideration.

4.4 Separation of the backing and adhesive is encouraged.

5.0 Significance and Use

5.1 Pyrolysis is a destructive analytical method; therefore, it is often placed at the end of an analytical scheme in which the combination of previous analytical techniques was incapable of discriminating samples. Since it may be able to add additional information that allows for discrimination between samples, its use is recommended for tape analysis and comparisons when sufficient sample is available.

5.2 Py-GC and Py-GC/MS are applicable to various polymer types. The pyrograms generated from Py-GC and Py-GC/MS can be used to compare the organic content of samples and to identify most of the major organic constituents in polymer samples, enabling classification. This entails analyzing reference standards and empirically assigning peaks in the pyrogram. When used for comparison, the goal is to determine whether any significant differences exist between the samples.

5.3 The use of two independent chromatographic columns (one high polarity and one low polarity) in Py-GC systems may provide improved sensitivity and complementary pyrograms (Saferstein).

5.4 Py-GC coupled with mass spectrometry is a very powerful and sensitive analytical technique that can be used to effectively characterize tape samples. The reconstructed total ion chromatogram in Py-GC/MS looks similar to a Py-GC chromatogram and provides comparable information to conventional Py-GC analysis. Additionally, Py-GC/MS provides information about the individual pyrolysis components of the pyrolyzate, which enhances the ability to chemically classify the different tape components. This entails analyzing reference standards and empirically assigning peaks in the pyrogram. The pyrolyzates produced are often not the same materials that were originally added in the manufacturing process prior to polymerization but frequently indicate the original materials.

6.0 Sample Handling

6.1 The general collection, handling, and tracking of samples shall meet or exceed the requirements of ASTM E 1492 as well as the relevant portions of SWGMAT's Trace Evidence Quality Assurance Guidelines Document.

6.2 The sample to be analyzed should first be examined with a stereomicroscope to ensure that the sample is free of any foreign material. Sample preparation should be carried out using a stereomicroscope, and clean tools must be used to handle the sample and the quartz tube or platinum foil. Samples to be compared should be prepared in the same manner resulting in approximately equivalent sizes and should be analyzed using identical instrument conditions.

6.3 Sample size is typically on the order of 10 to 150 micrograms, depending on instrument sensitivity and chemical composition of the material (e.g., amount of inorganic filler, type of elastomer), and should be approximately equivalent for all samples to be compared.

6.4 Removing the adhesive from a substrate for analysis can be done by rolling a metal probe along the tape, allowing the adhesive to collect on the probe. Alternatively, a scalpel can be used to tease up some of the adhesive. The collected adhesive is then transferred to the pyrolyzer sampling device using a scalpel, tweezers, or other suitable tool. The tool should be wiped clean with acetone or another suitable solvent between uses.

6.5 The backing can be analyzed separately. It can be sampled by removing the adhesive using an appropriate solvent, or thin peels can be taken from intact tape.

7.0 Analysis

The instrumental operating conditions should be optimized for the pyrolysis and chromatographic separation of pressure-sensitive tape components.

7.1 Pyrolysis Temperature

7.1.1 Temperature control of the pyrolysis process enables reproducibility of the polymer fragmentation.

7.1.2 The pyrolysis temperature must allow for its complete degradation without causing excessive bond breakage. Too much fragmentation will render the resulting pyrogram very difficult to interpret.

7.1.3 The pyrolysis unit must pyrolyze the sample at a set temperature and/or at a reproducible heating rate for a specific duration.

7.2 Gas Chromatograph Parameters

7.2.1 The gas chromatograph must have a reproducible temperature profile and a stable carrier gas flow rate.

7.2.2 Column type, gas-flow rates, and temperature programs influence the pyrograms obtained during analysis. The conditions should be chosen based on the quality of pyrograms they produce with regard to peak resolution and repeatability.

7.3 Mass Spectral Range

7.3.1 A scan range should be chosen in order to allow analysis of breakdown products of potentially large molecules, e.g., polymers, while disregarding lower molecular weight fragments that may unnecessarily clutter the mass spectrum. Usually the mass range starts between 30 and 50 mass units and ends about 500 to 650 mass units.

7.4 Example Experimental Conditions

Instrumental parameters will vary depending on the instrument system. The following parameters may be used as a starting point for Py-GC/MS analysis, but each laboratory should establish its own optimized parameters. The references in Section 10.0 can also be consulted for possible conditions.

7.4.1 Pyrolysis temperature and time: 700°C for 10 sec.

GC oven temperature program:

Interface temperature	275 °C
Column	non-polar capillary column (30 m 0.25 mm ID)
Carrier gas	Helium
Pressure	200 kPa
Split flow ratio	75:1
Oven program	Column remains at 40 °C for 2 minutes Ramp temperature 6 °C/min to 295 °C Hold at 290 °C for 5 min *Total run time: ~ 47 minutes*

Mass spectrometer:

Scan speed	Scanned 1000 m/z per sec
Time interval	0.5 Seconds
Mass range	m/z 50-500
Transfer line	290 °C

7.5 Quality control

Quality assurance and quality control procedures should be established and documented by the laboratory.

7.5.1 Sample introduction

7.5.1.1 Quartz tube

7.5.1.1.1 If using or reusing a quartz pyrolysis tube, it must be cleaned before each use. Each laboratory should develop, document, and use a cleaning procedure that demonstrates the container is free of contamination on subsequent runs.

7.5.1.1.2 Quartz tubes should be discarded when significantly damaged or residues have built up.

7.5.1.1.3 When inserting the quartz tube into the platinum coil of the pyrolysis unit, care must be taken to ensure even spacing of the coils along the length of the coil.

7.5.1.1.4 The position of the sample inside the quartz tube should be the same for all samples to ensure reproducibility. Samples may be retained in a fixed position in the tube by the addition of quartz wool or a filler post.

7.5.1.2 Other sample introduction containers/methods (specific to different types of pyrolysis units) may be used depending on the instrumentation.

7.5.2 Blanks

7.5.2.1 A system blank should be run prior to analyzing each sample (evidentiary and reference standard) to ensure and demonstrate that there is no contamination and/or carryover.

7.5.2.2 The system blank should include all aspects of the system, including the sample container.

7.5.2.3 Acceptable maximum peak heights in blank runs should be defined in laboratory procedures.

7.5.3 Performance Check
Prior to use, the performance of the instrument must be verified.

7.5.3.1 Instrument verification may be performed by analyzing a sample of a standard polymer or resin such as polyethylene, polystyrene, or Kraton 1107.

7.5.3.2 The standard that is used should demonstrate reproducible pyrolysis fragmentation, separation of peaks, and peak area ratios.

7.5.3.3 The frequency with which this is carried out should be documented in logbooks and laboratory procedures.

8.0 Interpretation

8.1 Classification/Identification of Polymeric Tape Components
Pyrolysis techniques are suitable for the identification of polymers by their pyrolysis products at specified measurement conditions. Combined with retention times, pattern of chromatographic peaks and mass spectra of pyrolysis products can be used to compare and to identify pyrolysis products.

8.1.1 Identification can be accomplished by comparison of a known sample, questioned samples, or both to a reference library or a contemporaneously analyzed reference sample.

8.1.2 The library chromatograms should originate from the same instrument and protocol used in the current analysis. When possible, the standards used in creating the library should be traceable reference standards.

8.1.3 When MS is employed, individual chromatographic peaks can also be identified via mass spectral library searches. The components identified may aid in determining the original starting materials of the manufacturing process.

8.2 Comparison

8.2.1 Comparison of the pyrograms can be accomplished side-by-side or through overlays.

8.2.2 There are a number of significant factors that should be considered when comparing pyrograms, including the presence or absence of peaks, retention times, shapes, and relative intensities. Additional sample replicates should be performed to evaluate reproducibility of these pyrogram characteristics.

8.2.3 The presence of additional peaks could come from true differences between the samples or from extraneous material adhering to the sample. If extraneous material is suspected as the source of the difference, the sample should be cleaned and additional replicates analyzed.

8.2.4 For pyrograms to be considered indistinguishable, the retention times of the peaks should have reasonable agreement with each other. Positions of corresponding peaks in two or more chromatograms being compared should be within a certain time frame of each other (e.g., ±0.1 minute, ±2%). An acceptable tolerance should be established by each laboratory and may be dependent on various factors such as the length of the chromatography program, the length of the column, and whether the peak is narrow or broad. For narrow peaks one may use tighter constraints, and with broad peaks the variation may be slightly greater.

8.2.5 For pyrograms to be considered indistinguishable, the retention time, and the intensity and shape of the peaks should be consistent between comparison samples. The peak width and the symmetry of each peak should be evaluated. In practice, very polar substances, for instance, often form broad peaks when using a non-polar column; in this case, the reproducibility of retention time, peak intensity, and peak shape may be relatively poor. Sample size may also affect the peak width and resolution.

8.2.6 For pyrograms to be considered indistinguishable, the relative intensities of the major respective peaks should be similar between comparison samples. The relative intensity may be affected by the heterogeneity and/or size of the sample. If replicate analyses are conducted, they could demonstrate a range of possible relative intensities.

8.3 Conclusions

Three conclusions can be reached after evaluating and comparing the pyrograms: 1) the pyrograms are dissimilar, 2) the pyrograms are indistinguishable, or 3) inconclusive.

8.3.1 The pyrograms are dissimilar if there is at least one significant, reproducible difference in the pyrograms. Significant differences are differences in the presence or absence of a peak or in relative peak intensities. These differences are too large to be explained by factors such as heterogeneity, contamination or poor reproducibility.

8.3.2 The pyrograms are indistinguishable if there are no significant differences in the pyrograms. Differences are not significant if the variation can be explained by factors such as heterogeneity, contamination, or poor reproducibility.

8.3.3 An inconclusive determination is reached if the significance of any possible difference(s) cannot be completely assessed, e.g., sample size constraints.

9.0 Documentation

9.1 When making comparisons of tape samples, similarity or dissimilarity in the pyrograms should be noted.

9.2 For chemical identification of tape components, the mass spectra must be compared to those of known reference materials.

9.3 Case notes should include a copy of all of the instrumental data that was used to reach a conclusion. All copies should include a unique sample designation, the operator's name/initials, and the date of analysis.

9.4 Case notes should also include a description of the evidence analyzed by Py-GC or Py-GC/MS, the method of sample preparation, and the analytical instrumentation used. In addition, the operating parameters used should be included in case notes or documented in the laboratory, accessible for later reference.

9.5 The following variables should be addressed in laboratory procedures or case notes:

Pyrolysis Conditions
- Pyrolysis unit used
- Interface temperature
- Ramp rate, if used
- Pyrolysis temperature
- Pyrolysis time

Gas Chromatography Conditions
- Instrument used
- Column used (including length, diameter, coating, coating thickness)
- Injector temperature
- Mobile phase/Carrier gas and flow rate
- Inlet pressure or flow (constant pressure or constant flow)
- Split mode/ratio
- Oven temperature (including initial and final temperatures, ramp rates, durations)
- Detector type
- Interface (transfer line) temperature

Mass Spectrometer conditions, if used
- Instrument used
- Ionization mode
- Mass range
- Scans/second

9.6 See SWGMAT's Trace Evidence Quality Assurance Guidelines for further requirements.

10.0 Bibliography

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