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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