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Standard Guide for Using Pyrolysis Gas Chromatography and Pyrolysis Gas Chromatography-Mass Spectrometry in Forensic Polymer Examinations[1]

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INTRODUCTION

The forensic analysis of polymers (for example, fibers, paints and coatings, tapes and adhesives) using pyrolysis gas-chromatography (PGC) or pyrolysis gas-chromatography/mass spectrometry (PGC/MS) is a destructive technique that provides detailed organic chemical information about such samples. This information augments 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).

1. Scope

1.1 This guide covers information and recommendations for the selection and application of various PGC and PGC/MS procedures and methods in the forensic examination of polymeric materials (for example, fibers, paint, tape). PGC and PGC/MS methods are used for the identification and comparison of the organic components of these materials. Refer to Practice D3452 for further information on the preparation of the pyrolysis system for polymeric analyses.

1.2 This guide is to be used in conjunction with a broader analytical scheme such as Guides E1610 or E3260, or the SWGMAT Forensic Fiber Examination Guidelines.

1.3 This standard is intended for use by competent forensic science practitioners with the requisite formal education, discipline-specific training (see Practices E2917, E3233, E3234), and demonstrated proficiency to perform forensic casework.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D16 Terminology for Paint, Related Coatings, Materials, and Applications

D123 Terminology Relating to Textiles

D3452 Practice for Rubber—Identification by Pyrolysis-Gas Chromatography

E355 Practice for Gas Chromatography Terms and Relationships

E1492 Practice for Receiving, Documenting, Storing, and Retrieving Evidence in a Forensic Science Laboratory

E1610 Guide for Forensic Paint Analysis and Comparison

E1732 Terminology Relating to Forensic Science

E2917 Practice for Forensic Science Practitioner Training, Continuing Education, and Professional Development Programs

E3233 Practice for Forensic Tape Analysis Training Program

E3234 Practice for Forensic Paint Analysis Training Program

E3260 Guide for Forensic Examination and Comparison of

[1] This guide is under the jurisdiction of ASTM Committee E30 on Forensic Sciences and is the direct responsibility of Subcommittee E30.01 on Criminalistics.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

Pressure Sensitive Tapes

2.2 *Other Documents:*

ISO/IEC 17025 General requirements for the competence of testing and calibration laboratories[3]

SWGMAT Forensic Fiber Examination Guidelines[4]

SWGMAT Trace Evidence Quality Assurance Guidelines[4]

SWGMAT Trace Evidence Recovery Guidelines[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this guide, see Terminologies D16, D123, and E1732, and Practice E355.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *Curie point, n*—the temperature at which a ferromagnetic metal loses its ferromagnetic properties.

3.2.2 *exclusionary difference, n*—a difference in a feature or property between compared items that is substantial enough to determine that they did not originate from the same source.

3.2.3 *interface temperature, n*—the temperature of the heated zone between the pyrolysis unit and the GC.

3.2.4 *pyrogram, n*—a chromatogram obtained from the pyrolysis products of a material.

3.2.5 *pyrolysis, n*—the thermal fragmentation of a substance in an inert atmosphere.

3.2.6 *pyrolysis temperature, n*—the temperature (set or ramped) at which the pyrolysis of the sample is performed.

3.2.7 *pyrolyzate, n*—the product of the pyrolysis process.

3.2.8 *traceable reference standard, n*—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.

4. Significance and Use

4.1 This guide provides guidance in the selection of appropriate sample preparation methods and instrumental parameters for the analysis, comparison, or identification of various polymeric materials by PGC and PGC/MS.

4.1.1 PGC/MS can differentiate between classes of fibers (for example, acrylic, polyester, nylon) and within classes of fibers (for example, acrylics) (**1-3**).[5]

4.1.2 Paint binders are differentiated based upon the variety of monomers used in paint formulations which could be difficult to identify by other analytical techniques. In addition, some additives can be detected or identified.

4.1.3 Differentiation can be achieved by the separation and identification of organic components in the adhesive portion of tapes (**4, 5**) and in the backings of electrical tapes (**6**).

4.1.4 PGC/MS can provide additional discrimination for other types of polymers such as automotive lenses, automotive body fillers, cosmetics, plastics, and rubbers (**7-9**).

4.2 Pyrolysis breaks a large molecule into many smaller molecules in a reproducible fashion through the breaking of bonds by means of the application of thermal energy. Analytical pyrolysis is used to provide chemical information on organic-containing solids that cannot be dissolved or otherwise introduced into a chromatographic system. It is also used to analyze and compare solvents bound in a solid material (such as tape adhesives) (**10**). When analyzed using a separation technique such as gas chromatography, the smaller molecules produced through the action of pyrolysis form a pattern of separated fragments. Mass and structural information indicative of the original molecule are also available when a mass spectral detector is used.

4.3 Although a destructive method, and therefore often placed at the end of an analytical scheme, the pyrograms produced from different polymer compositions form characteristic patterns that are useful for both identification of polymer type and comparisons between samples (**4, 6, 9-23**). When used for comparison purposes, the goal is to determine whether any exclusionary differences exist between the samples.

5. Sample Handling

5.1 *General Considerations:*

5.1.1 Practice E1492 as well as the relevant portions of the SWGMAT Trace Evidence Quality Assurance Guidelines and Trace Evidence Recovery Guidelines are followed for the general collection, handling, documentation, and tracking of specimens and samples.

5.1.2 Since PGC is a destructive technique, considerations are made prior to analysis to ensure that the entire sample is not consumed.

5.1.3 Prior to sampling, any foreign debris or contaminants that are visually observed by stereomicroscopy should be scraped away or otherwise removed.

5.1.4 Except where sample size or condition makes it prohibitive, samples for PGC or PGCMS analysis are prepared in a manner that permits resolution and analysis of individual layers. This allows the organic components from each layer to be effectively characterized and attributed to the appropriate layer. When samples are too small to isolate individual layers, samples from multiple layers can be analyzed simultaneously. Samples for comparison are prepared under the same conditions and in the same manner whenever possible.

5.1.5 Sample size can vary in accordance with polymer type, pyrolysis method, column type, chromatographic conditions, and detection methods. As a general approach, varying amounts of a known polymeric material can be analyzed to determine the minimum amount that provides sufficient signal to identify the characteristic components. Once optimal sample size is determined, samples of similar size and shape should be used for analyzing replicates and for comparison purposes. Instrument manufacturer recommendations and published studies of like materials can be used for guidance in determining approximate sample size.

5.1.6 Samples are positioned on or within appropriate sample holders to maximize pyrolysis. More specific guidance on sample holders is discussed in 6.7.1.

[3] Available from International Organization for Standardization (ISO), ISO Central Secretariat, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, https://www.iso.org.

[4] Available from Scientific Working Group for Materials Analysis (SWGMAT), http://swgmat.org.

[5] The boldface numbers in parentheses refer to a list of references at the end of this standard.

5.2 *Fibers:*

5.2.1 Pyrolysis should be conducted on individual fibers, when possible. Optimal results are obtained from fiber lengths of 1–2 cm, although fibers as small as a few mm in length can be analyzed. As little as 25–30 µg has been reported to be sufficient for some acrylic fibers (**1**).

5.3 *Paint:*

5.3.1 Suitable paint sample sizes for pyrolysis range from 5–150 µg (**21**, **24**). Generally, more sample should be used when the layer is heavily filled with inorganic material.

5.4 *Tape:*

5.4.1 Suitable tape sample sizes for pyrolysis range from 10–60 µg, depending on the type of tape as well as the chemical composition of the material (for example, amount of inorganic filler, type of elastomer). A 0.5 mm square of electrical tape has been reported to correspond to approximately 25 µg (**21**).

5.4.2 Adhesive can be removed from tape for analysis using several methods. When preparing the adhesive for analysis, care should be taken to make sure any reinforcement materials (that is, fibers) are not present in the sample.

5.4.3 The tape backing can be isolated for analysis by removing the adhesive using a metal probe, a scalpel, an appropriate solvent, or a combination of these methods. Alternately, a thin peel of the tape backing can be used. The thin peel should only be used if the backing is known to consist of a single layer polymer.

5.5 *Other Polymeric Materials:*

5.5.1 Suitable sample sizes for pyrolysis of other polymeric materials generally range from 10–100 µg (**25**), with automotive lens and rubber samples closer to 100 µg and cosmetic samples approximately 25–50 µg (**7**, **16**, **26**).

6. Instrumentation and Operating Conditions

6.1 PGC instrumentation consists of two distinct components: (*1*) the pyrolysis unit, where sample fragmentation occurs, and (*2*) the gas chromatograph where separation and detection of the pyrolyzate fragments occur. In instances where a mass spectrometer is the detector, it is considered to be a third distinct part of the instrument, as it aids in the identification of selected pyrolyzates. Some systems include an interface between the pyrolysis unit and the gas chromatograph.

6.2 The two most common detectors for use with PGC include the flame ionization detector (FID) and mass spectrometer (MS).

6.2.1 The FID is capable of detecting a broad range of combustible pyrolyzates. It is relatively inexpensive and has a large linear dynamic range. Identifications and comparisons with data from an FID are based on retention times of peaks and the appearance of overall pyrogram patterns.

6.2.2 The MS provides information about the individual fragments of the pyrolyzates, which enhances the ability to chemically classify the different polymer components. By selecting ions of interest, classes of compounds are able to be selectively viewed and searched for specific compounds.

6.2.2.1 Various types of mass spectrometers are available for use as GC detectors.

6.2.2.2 An electron ionization source is recommended instead of a chemical ionization source for applications discussed in this guide.

6.2.3 Reconstructed total ion chromatograms in PGC/MS look similar to PGC chromatograms and provide comparable information to conventional PGC analysis.

6.3 *Pyrolysis Systems:*

6.3.1 Three different types of pyrolyzers are available: (*1*) resistively-heated, (*2*) Curie point/inductively-heated, and (*3*) microfurnace.

6.3.2 In resistively-heated pyrolysis, the coil heats first, then transfers the heat through the sample holder (for example, quartz tube) and heats the sample (**27**). Temperature ramping is possible and the desired temperature can be selected by controlling the current. The coil reaches its final temperature in 1–2 seconds; however, it can take several seconds for the sample to pyrolyze for a total wait time close to 10 seconds. Some drawbacks are that coil probes can exhibit "cold spots" and the coil is slow to heat the thermal mass of the quartz tube when compared with other pyrolysis systems.

6.3.3 With inductively-heated or Curie point pyrolysis, the sample is either coated on or placed in a ferromagnetic wire, ribbon, or boat. The type of wire, ribbon, or boat that is used determines the maximum temperature that can be reached. Different alloy compositions are available for a wide range of temperatures. Temperature ramping is not an option with this technique.

6.3.4 Microfurnace pyrolyzers use a quartz or metal cup to introduce the sample into the heated analytical chamber (microfurnace). The microfurnace is typically held at a single temperature without the need for equilibration; this allows for greater reproducibility than observed with other pyrolysis systems. The thermal mass of the cup is negligible compared to the microfurnace, so the cup and sample reach the set temperature nearly instantaneously.

6.4 *Pyrolysis Temperature:*

6.4.1 The pyrolysis unit should use a temperature that results in complete pyrolysis without causing excessive bond breakage or fragmentation. Excessive fragmentation leads to a commonality of fragmentation data in the resulting pyrogram and difficulties in classification, identification, or discrimination.

6.4.2 The same analysis conditions (for example, set point, heating rate, time) are used for samples being compared.

6.5 *Instrument Operating Parameters:*

6.5.1 Operating conditions (for example, time, column selection, temperature programming) are optimized for pyrolysis, chromatographic separation, and detection. As the analyst determines specific analytical needs, actual operating conditions can vary. Variation of the operating values is permitted. The choice of conditions is based on the quality of pyrograms produced with regard to peak separation, resolution, and reproducibility.

6.5.2 *Inlet Temperature*—Typical inlet temperatures range from 200–300 °C.

6.5.3 *Split Ratio*—The sample introduced into the instrument is split so that neither the column nor detector are

saturated by the sample. Typical split ratios range from 20:1 to 100:1, depending on sample size.

6.5.4 Oven parameters are critical for separation of pyrolyzates. Oven temperature, ramp rates, column type, and gas flow rates influence the pyrograms obtained. Molecular weight, resolution between peaks, potential for sample carryover, and total run time, are considered when selecting these parameters.

6.5.4.1 Temperature ramps should be used, as samples can contain a wide range of fragment sizes.

6.5.4.2 A defined temperature profile is used as well as a stable carrier gas flow rate.

6.5.4.3 Column carrier gas flow rates affect make-up gas flow rates. Therefore, for PGC with FID, manufacturers recommended flow rates are used for hydrogen and oxygen.

6.5.5 The choice of GC column is dependent upon the polarities of pyrolyzates (**28**, **29**). The use of two independent chromatographic columns (one high polarity and one low polarity) concurrently in a single PGC system can provide improved sensitivity and complementary pyrograms (**28**).

6.6 *Example Instrumental Parameters*—The following suggested operating conditions are meant as general guidance for PGC/MS analysis using a resistively-heated probe; however, parameters are optimized for each instrument. Additional examples of instrumental conditions are available in a variety of references (**1**, **3**, **5-7**, **10-12**, **16**, **27**, **28**, **30-32**).

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
Mass spectrometer:
    Scan speed: 1000 m/z per sec
    Time interval: 0.5 seconds
    Mass range: 50–500 m/z
    Transfer line: 290 °C
Total run time: ~ 47 minutes

6.7 *Quality Control:*

6.7.1 *Sample Holders:*

6.7.1.1 Reusable sample holders (for example, quartz tube, cups, or metallic ribbon) are cleaned before each use and have been demonstrated to be free of contamination on subsequent runs. One method for cleaning sample holders includes heating them in an apparatus (for example, hand-held propane torch, muffle furnace, filament coil) prior to use.

6.7.1.2 Containers are discarded if they are damaged or significant residues are observed. Generally, the residues left behind are inorganic components that can be characterized using other techniques, if desired.

6.7.1.3 For coil pyrolysis probes the coils are evenly spaced by gently adjusting them with forceps. All samples are placed in the same position inside the sample holder to ensure reproducibility. In the case of quartz tubes, samples can be held in position in the tube by the addition of quartz wool or a filler post.

6.7.2 *Blanks:*

6.7.2.1 A system blank is run using all aspects of the system prior to every case sample to ensure that there is no contamination or carryover.

6.7.2.2 The system blank is evaluated against acceptance criteria for blank runs in laboratory procedures. An ideal blank exhibits no peaks. Any peaks observed in a system blank are evaluated to determine the acceptability of the blank.

6.7.3 *Performance Check:*

6.7.3.1 For PGC/MS, the mass spectrometer is tuned using a standard reference compound (for example, perfluorotributylamine) to ensure optimization of peak shape, accurate mass assignments, and sensitivity.

6.7.3.2 Prior to casework samples, a standard polymer (for example, polyethylene, polystyrene, Kraton D1107) is analyzed using the same analytical conditions. The pyrogram produced by the standard is evaluated to ensure it meets the laboratory's established quality control criteria such as demonstration of reproducible separation of peaks, peak area ratios, and pyrolysis fragmentation.

7. Identification, Comparison, and Interpretation

7.1 *Identification:*

7.1.1 Identification of polymers by PGC or PGC/MS is based on the interpretation of pyrograms and comparison to polymer references. In combination, retention times, chromatographic peak patterns, and mass spectra can be used to identify and to compare pyrolysis products.

7.1.2 A sample pyrogram is compared to a reference library or a contemporaneously analyzed reference material to identify a polymer (**25**).

7.1.3 Optimal library pyrograms originate from the same instrument and protocol used in the current analysis. Traceable reference standards should be used in creating the library.

7.1.4 When MS is employed, individual chromatographic peaks can be identified by means of mass spectral library searches. The components identified could aid in determining the original starting materials of the manufacturing process.

7.2 *PGC or PGC/MS Pyrogram Comparison:*

7.2.1 PGC or PGC/MS pyrogram comparisons should be conducted between pyrograms collected using similar sample preparations, similar sample characteristics (for example, thickness, topography), and similar instrumental parameters, as appropriate.

7.2.2 Pyrograms are compared and interpretated based on the observation of any differences, or lack thereof, between the sets of PGC or PGC/MS data.

7.2.2.1 Pyrogram overlay can be used for comparing data where the presence or absence of peaks, peak shapes, and relative intensities are all considered in the evaluation as to whether exclusionary differences exist between compared samples.

7.2.2.2 When assessing differences between pyrograms, consider sample limitations (for example, small samples, thin layers, dirty samples, sample smears that eliminate layer structure) and instrumental limitations (for example, sampling size, limits of detection).