

Pyrolysis Gas Chromatography/Mass Spectrometry Analysis of Paints, Tapes, and Polymers

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1 INTRODUCTION

This document describes the sample preparation and suggested instrumental parameters for the Pyrolysis Gas Chromatography/Mass Spectrometry (Py-GC/MS) analysis of paints, tapes, and polymers.

2 SCOPE

This procedure applies to Chemistry Unit caseworking personnel who analyze paints and polymers via Py-GC/MS.

3 EQUIPMENT

- A. Instrumentation - Gas Chromatograph, Mass Selective Detector with EI Source, and Software (Agilent or equivalent)
- B. Autosampler - Pyrolysis Autosampler, accessories, and software (Frontier or equivalent)
- C. Sample holder - alloyed metal cups (Frontier or equivalent)
- D. Polymeric reference materials (Scientific Polymer Products, Inc. or equivalent)
- E. Stereo-microscope (~ 6 to ~ 50x) with appropriate lighting
- F. General Laboratory Supplies

4 STANDARDS AND CONTROLS

4.1 Performance Check

Refer to IOSS-711 for details on the performance checks and necessary supplies to conduct these checks and operate the instrument.

4.2 Controls

Manufacturer-supplied and commercially available paints, tapes, polymers, adhesives, and sealants are maintained within the FBI Laboratory. These materials are used in casework in accordance with CHEM-100.

5 SAMPLING

Refer to the current version of the relevant material's General Approach technical procedure (e.g., PP-800, PP-801, PP-802) for guidance as to how samples are selected for analysis and comparison. Record the sample(s) selected for analysis in the case notes.

6 PROCEDURE

6.1 Sample Prep

1. Using a scalpel or similar tool, prepare a clean sample of material of sufficient size (approximately 50 µg) to provide an adequate signal. The amount can vary depending on instrument sensitivity and chemical composition of the material (e.g., amount of inorganic filler, type of binder).
 - i. Separate individual components (e.g., paint layers, backings, adhesives) by taking thin peels with a scalpel.
 - ii. Multi-layer samples can be analyzed if it is not possible to separate layers.
2. If appropriate, sample dried material (e.g., cured spray paint on the nozzle) from the container of an uncured specimen.
 - i. Alternatively, a portion of an uncured sample (e.g., glues, two-part adhesive systems, liquid paint) can be mixed, applied to a clean microscope slide or other suitable substrate, and permitted to cure/harden according to the manufacturer's recommendations.
3. Place the sample in an appropriate container for analysis. Proper and consistent placement of the sample within the base of the sample cup is critical for complete pyrolysis and reproducibility of data.

6.2 Instrument Usage

1. Refer to IOSS-711 to verify that the daily and monthly performance monitoring procedures have been appropriately conducted and recorded in the instrument log and case notes.
2. Analyze the performance standard, sample(s), and blanks using the suggested instrumental parameters that follow. At a minimum, one blank is placed before each standard, sample, or reference material analyzed.
3. If identification of the pyrolyzates is warranted, known standards can be analyzed under the same instrumental conditions used for sample analysis.

7 INSTRUMENTAL CONDITIONS

The following instrumental conditions are a guide for all standards and samples and are set within the instrument method but are not necessarily exact values. The same conditions will be used for all samples that are compared to one another as well as for the blanks that precede these samples. The method used is retained with the case record (e.g., printed and stored in the case notes).

7.1 Pyrolysis GC

Pyrolysis Autosampler:

Interface Set Point: 300°C

Furnace Temp: 600°C

Furnace Hold Time: 0.20 min

GC Oven:

Initial Temp: 50°C

Initial Time: 2 minutes

Ramp Rate: 13°C/minute

Final Temp: 325 °C

Final Hold Time: 15 minutes

Run Time: 38.154 minutes

GC Inlet:

Mode: Split

Split Ratio: 50:1

Inlet Temp: 300°C

Split Flow: 35 mL/min

Carrier: Helium

Init Flow: 0.7 mL/min

Flow Mode: Constant flow

Septum purge: 3 mL/min

GC Column:

Type: HP-5 or equivalent

Length: 30 m

Diameter: 250 µm

Film Thickness: 0.25 µm

7.2 MS Parameters

Source Temp: 230°C

Ionization Mode: Electron Impact (EI mode)

Transfer Line Temp: 300°C

Scan Mode: Full Scan

Scan Range: 34-650 m/z

8 ACCEPTANCE CRITERIA

The following criteria are used as a guide in determining the acceptability of the data produced in this procedure. Retention time, peak shape, relative intensity, and the presence/absence of corresponding diagnostic peaks are all evaluated. Examples of diagnostic peaks would be those that aid in the classification or identification of the polymer based on the components present.

8.1 Blanks

The blank run before each sample is evaluated for the presence of carry-over peaks from the previous sample. It is also evaluated for system peaks that could contribute to a sample's signal, possibly hindering appropriate evaluation of true peaks that are present. Ideally, the blank preceding the sample should not exhibit any chromatographic peaks greater than the CO₂ response. If extraneous peaks are noted, document that the peak was considered as well as the results of the evaluation.

8.2 Samples

1. Chromatography

- Peaks should show good chromatographic characteristics, with reasonable peak shape, width, and resolution.
- The retention time of a peak should be within $\pm 2\%$ when compared to a contemporaneously analyzed reference standard (e.g., Polystyrene).

- The signal intensity for a peak should be at least 10x greater than the intensity for any carryover peak which is present in the preceding blank.

2. Mass Spectrometry

- The mass spectrum of the analyte of interest should be assessed against a contemporaneously analyzed reference standard (e.g., Polystyrene), library spectrum, or spectrum published in a peer reviewed reference.

3. Characterization

- For characterizations of an unknown sample, compare the data (pyrogram and mass spectrum) for the unknown sample with respect to a known reference material or mass spectral library.

4. Comparison

- Compare pyrograms of samples collected using similar preparations, sample characteristics (e.g., quantities, single layers vs multilayered samples), and instrumental parameters, as appropriate.
- Compare pyrograms side-by-side or using overlays.
- Interpret pyrograms based on the observation of chromatographic or spectral differences, or lack thereof, between the sets of data. Record observations and interpretations in the case notes or on the data printouts.
- As applicable, assess reproducibility of the pyrolysis process through the analysis of replicates.
- When assessing differences between pyrograms, consider sample limitations (e.g., small samples, dirty samples) and instrumentation limitations (e.g., sampling size, limits of detection).
- The presence of additional peaks could be inherent differences between samples, from contamination or carry-over, or system peaks (e.g., siloxanes). Document that the peak was considered and the possible explanations for why those peaks were present. If the additional peaks are explainable as contamination, carry-over, or system peaks, then they are not exclusionary differences.
- Possible reasons for chromatographic or mass spectral differences include dissimilar sample conditions (e.g., quantities, contamination from adjacent layers), lack of representativeness of the specimen or source material, contribution from extraneous materials, or origination from different source materials. Additional samples can sometimes provide supplemental data to assist in assessing such differences.
- If suitable pyrograms are produced, comparisons can provide information regarding the potential relationship of the sources of the samples.

9 LIMITATIONS

- Py-GC/MS is a destructive analytical technique.
- Sample size or condition may preclude examination by this technique.
- The information obtained from the analysis of combined layers of a multi-layer paint chip will hinder the ability to discriminate between the individual layers.

10 PRECAUTIONARY STATEMENTS

- As with any procedure involving trace evidence, ensure actions minimize the potential for loss or contamination of the sample.
- When conducting comparative analysis of two or more samples, care must be taken to ensure that each specimen to be compared is present in approximately the same amount. Unequal sampling can result in relative intensity differences within this analytical technique.
- In a multi-layer material, care must be taken to ensure that each specimen is free of contribution from unwanted adjacent layers.
- Care must be taken during sample preparation to ensure consistency of sample placement within the bottom of the sample vessel.

11 REFERENCES

CHEM-100, Chemistry Unit, FBI Laboratory

IOSS-711, Research Support Unit, FBI Laboratory

PP-800, Chemistry Unit, FBI Laboratory

PP-801, Chemistry Unit, FBI Laboratory

PP-802, Chemistry Unit, FBI Laboratory

12 REVISION HISTORY

Revision	Issued	Changes
08	07/31/2023	Corrected IOSS-715 to IOSS-711.
09	01/02/2025	Streamlined equipment list and corrected formatting errors.