I. Scope

Pyrolysis is a technique used to break chemical bonds of molecules by the use of thermal energy only. Analytical pyrolysis is a technique to study molecules by observing their behavior during pyrolysis and the resulting molecular fragments.

Pyrolysis breaks large molecules in the pyrolysis chamber within a short period of time into smaller fragments, which are called pyrolysates. During pyrolysis, helium gas is constantly flowing through the pyrolysis chamber providing an inert atmosphere. This constant flow of helium carries the pyrolysates form the pyrolysis chamber into the GC column for separation and then the GC separated pyrolysates are sorted and detached by MS. A program (reconstructed total ion chromatogram) is acquired which represents the separated pyrolysates. Pyrolysis is a well-known and widely accepted technique in the field of forensic science.

II. References

Wampler, Thomas P, Applied Pyrolysis Handbook, Marcel Dekker, Inc., New York, 1995

Irwin, William J., Analytical Pyrolysis-A Comprehensive Guide, Chromatographic Sciences Series, Vol. 22, Marcel Dekker, inc., New York, 1982

CDS Analytical, Inc., Pyrolysis Application Review

Wampler, T. P. and Levy, E. J., "Reproducibility in Pyrolysis, Recent Developments," *Journal of Analytical and Applied Pyrolysis,* 12, 1987, pp 75-82

Saferstein, R. "Forensic Analytical Pyrolysis", *Proceedings of the International Symposium on the Analysis and Identification of Polymers* 1984, pp 9-18

III. Apparatus/Reagents

The following are starting parameters. Depending on the sample, these may be changed:

Pyrolyzer:

1. Interface temperature: 200° C
2. Pyrolysis conditions: 750° C for 15 seconds
3. Clean: 1000° C for 5 seconds
4. Dry: 50° C for 60 seconds

Gas Chromatograph:

1. Column: Supelco MDN-5S capillary column 30m x 0.25mm ID x 0.25μm (or equivalent)
2. Carrier gas: Helium
3. Split ratio: 85:1

Oven temperature program:

1. Initial temperature: 40° C
2. Initial hold time: 1.00 minute

3. Ramping rate: 20°C/min
4. Final temp: 280° C
5. Hold: 7 minutes
6. Total run time: 20 minutes
7. Inlet temp: 280° C
8. Carrier: Chromatographic grade helium
9. Flow rate: Constant velocity at 40cm/secf

Single Quad Mass Spectrometer:

1. Ionization mode: Electron ionization
2. Mass range: 33-350 amu
3. Scans/sec: 2.35
4. Hold for 0.5 minutes before the filament turns on
5. Source temp: 160° C
6. Transfer line: 280° C
7. EI energy: 70 eV

Kraton Standard

An approximate 20mg/ml solution of Kraton (isoprene/styrene//84/14) in toluene.

IV. Procedures

Tune

The mass spectrometer should be tuned and calibrated properly either by automatic tune or manual tune. A hard copy of the tuning report should be placed in the logbook for keeping track of the performance of the instrument.

Blanks and Standard

A blank run of pyrolysis of the quartz tube with the quartz wool must be acquired to ensure a contamination free system.

After the instrument is checked out as a problem free system, the Kraton standard is pyrolyzed to check the performance of the system. The data acquired for Kraton should be comparable with the standard in the binder with the three major peaks (isoprene, styrene and dipentene) of Kraton. The retention time should not vary more than 1% in these peaks unless conditions in the system have changed. The ratio of relative intensities should be as follows:

Isoprene/styrene: 50±10
Dipentene/Styrene: 60±10

Preparation/Loading of Kraton standard or Soluble Solids

The Kraton standard is prepared by dissolving the proper amount of solid kraton sample in toluene.

1µL of Kraton standard is delivered with a syringe onto the quartz wool inside the quartz tube. After loading the sample into the quartz tube, do a final visual examination to ensure that the sample will be in the center of the filament coil. This step ensures the uniform heating would be transferred to the sample. Then, a few minutes is allowed to air-dry the sample before loading

it onto the pyrolysis interface.

Solid Sample Preparation
Solid samples should be between 10 and 100µg. It is critical that all tools for sample preparation are clean; otherwise contamination could lead to inaccurate results. The analyte must be placed inside the quartz tube where uniform heat can be applied.

A. Comparative analysis: Comparison of a known sample to a questioned sample
For ensuring the best results, it is very important to have the samples in the same size and geometry. (Note: this can be done by cutting all samples before pyrolyzing any sample).

Ensure the instrument operates properly by looking at the mass spectrometer tuning report. No air leaks in GC or pyrolysis systems should be observed.

Check the instrument performance using the Kraton standard. (Note: If different operating parameters than above are used the Kraton standard will vary in pyrolysis product abundance and not correspond with the stated tolerances. In this instance comparison to an authentic standard will suffice)

Make sure to run the questioned and known samples under exactly the same conditions, and run blanks (quartz tube containing quartz wool) between samples.

Instrument performance should be monitored whenever any maintenance or repair is done to the system.

B. Identification analysis: Comparison of a known and/or questioned sample to a reference library
Follow all the steps stated in Section A.

Compare the programs of the questioned samples to the ATF's authentic reference library. Identifications can be made by running an authenticated reference standard if available.

CAUTION: Be very careful with handling the filament. The filament of the pyroprobe is made of platinum and can be easily distorted through improper handling. The temperature of the filament is dependent on the resistance of the platinum, and will be adversely affected of the filament is bent or damaged. In addition, bending the coil so that the loops tough each other, or the side of the probe body, will cause the probe to short circuit, overheating and damaging the filament. Always be sure to gently insert the quartz sample tube straight into the coil to minimize the chance of coil damage. NEVER operate the pyroprobe if the coil is touching the side of the probe body or if the coil has been compressed so that the loops are touching. The coil must be straight and centered, and the coils must be evenly spaced apart.

V. Quality Assurance

The mass spectrometer must be autotuned (calibrated) before analyzing samples to ensure the MS operates properly, and then the Kraton standard must be run to ensure the overall conditions of the instrument are proper. Once the pyrolysis of samples has started, the mass spectrometer only needs to be calibrated once a week.

VI. Safety Precautions

Proper cotton gloves need to be worn when inserting/removing the probe because the pyroprobe interface is very hot.

All gas cylinders must be properly secured, and pressure regulators should be inspected whenever cylinders are replaced.

Any maintenance should be done by someone who is familiar with the system.

Precautions need to be taken whenever working with chemicals which could pose potential health hazards.

Avoid direct contact with the heating coil when cleaning the quartz tube between runs. The filament coil is very hot (at 1000°C) during cleaning process and can cause serious burns.

VII. Glossary

- Pyrolysis: fragmentation of large molecules or polymers with thermal energy
- GC/MS: gas chromatography mass spectrometry
- Pyrogram (in conjunction with the GC/MS): reconstructed total ion chromatogram for a pyrolyzed sample
- Pyrolysate: neutral fragments resulting from pyrolysis