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 from the pyrolysis chamber into the GC column for separation and then the GC separated pyrolysates are sorted and detected by MS. A program (reconstructed total ion chromatogram) is acquired which represents the separated pyrolysates.

II. References

1) Wampler, Thomas P, Applied Pyrolysis Handbook, Marcel Dekker, Inc., New York, 1995
2) Irwin, William J., Analytical Pyrolysis-A Comprehensive Guide, Chromatographic Sciences Series, Vol. 22, Marcel Dekker, inc., New York, 1982
3) CDS Analytical, Inc., Pyrolysis Application Review
4) Wampler, T. P. and Levy, E. J., "Reproducibility in Pyrolysis, Recent Developments," *Journal of Analytical and Applied Pyrolysis*, 12, 1987, pp 75-82
5) Saferstein, R. "Forensic Analytical Pyrolysis", *Proceedings of the International Symposium on the Analysis and Identification of Polymers* 1984, pp 9-18
6) SWGMAT Paint Analysis and Comparison Guidelines http://www.swgmat.org/paint.htm
7) SWGMAT Guideline for the Forensic Examination of Pressure-sensitive Tapes - http://www.swgmat.org/tape.htm

Validation

PyGC-MS is a well known and scientifically accepted method for the identification, analysis and comparison of many types of trace evidence. Relevant examples of the broad nature of the method and related literature can be found in Section II (References).

III. Safety Precautions

1) Since the pyroprobe interface is very hot, hand protection should be used when inserting or removing the pyroprobe.
2) All gas cylinders must be properly secured, and pressure regulators should be inspected whenever cylinders are replaced.
3) Precautions need to be taken whenever working with chemicals which could pose potential

health hazards.

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

IV. Apparatus/Reagents:

PyGC-MS
Kraton standard (isoprene/styrene/84/14)
Quartz wool/ quartz tubes

Tune and Performance Check

The mass spectrometer must be tuned and the performance must be checked properly either by automatic tune or manual tune within 30 days of use. A hard copy of the tune report should be placed in the logbook for keeping track of the performance of the instrument.

Blanks

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

Kraton Standard

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 compared with the three major peaks (isoprene, styrene and dipentene) of the Kraton standard in the binder. The retention time should not vary more than 2% in these peaks unless conditions in the system have changed.

At a minimum, a Kraton standard is run when starting a case and ending a case to insure that the instrument is operating properly. If the case samples are analyzed over a number of days, the ending Kraton standard can be run after the last sample on the last day. The Kraton standard may be in solid or solution form. Other standards may be used as deemed necessary. The hard copy of the standards should be placed in the case notes.

Logbooks will be kept which document the performance of the calibrations as well as maintenance on the instrument.

V. Procedures

Sampling and Sample Preparation

Liquid samples:

On average, a 1µL sample of the liquid 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. Allow sample to dry before loading it onto the pyrolysis interface.

Solid Samples:
Sample size is sample dependant; however the same size should be used for all samples being compared. Most samples are between 50 and 100 micrometers. 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 with quartz wool where uniform heat can be applied.

Comparative Analysis - Comparison of a known sample to a questioned sample:
For ensuring the best results, it is very important to have samples of the same size and geometry.

Identification analysis: Comparison of a known and/or questioned sample to a reference standard:
Identifications can be made by running an authenticated reference standard or by comparing the sample to an authenticated standard reference library.

An instrument operating parameters form must be filled out when the PyGC-MS is used in casework (at least one per case). This form should be included in the case notes.

Troubleshooting:
Ensure the instrument operates properly by turning on the instrument and looking at the mass spectrometer tune page set at mass 4/18/28/32. No water/air leaks in GC the systems should be observed.

Check the instrument performance using the Kraton standard.
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.

PRECAUTIONS: 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 if the filament is bent or damaged. In addition, bending the coil so that the loops touch 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.

VI. Quality Assurance

Through regular performance checks, use of known standards, and upkeep of instrument logbooks the quality of the PyGC-MS method is assured

There is no known error rate for this type of examination.