Technical Procedure for Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC-MS)

1.0 Purpose – This technical procedure shall be followed for the operation of the pyrolysis-gas chromatograph-mass spectrometer (Py-GC-MS).

2.0 Scope – This procedure applies to all Py-GC-MS instruments in the Trace Unit.

3.0 Definitions – N/A

4.0 Equipment, Materials and Reagents

4.1 Equipment

- Agilent 6890 Gas Chromatograph with Agilent 5975B Mass Selective Detector
- CDS Analytical 1500 Manual Injection Pyrolysis Unit

4.2 Materials

- Quartz tubes
- Quartz wool
- Digital Flow Meter
- Stainless Steel nut septa
- GC inlet septa
- Probe septa
- Tweezers
- A non-polar capillary column with a (5 %-Phenyl)-methylpolysiloxane stationary phase such as a DB-5 or HP-5
- Polyethylene Standard
- PFTBA

4.3 Reagents – N/A

5.0 Procedure

5.1 Start-up and Performance Checks

5.1.1 The Py-GC-MS shall be kept on at all times.

5.1.2 Performance Check using the Autotune program:

5.1.2.1 Each day that the instrument is used, the performance of the MS shall be checked. The performance check is required once per day. If the instrument is not being utilized on a particular day, the daily Autotune shall not be required.

5.1.2.2 This procedure uses perfluorotributylamine (PFTBA) as a tuning standard and the resulting tune report shall be electronically archived.

5.1.2.3 The Autotune report shall be compared to previous ones and major variations which may indicate instrument problems shall be addressed.

5.1.2.4 The parameters for a passing Autotune are as follows:

5.1.2.4.1 The three tuning masses in the upper profile part of the report shall be within +/- 0.2 amu of 69.00, 219.00, and 502.00.

5.1.2.4.2 The peak widths of these three peaks shall be 0.60 +/- 0.1 amu.

5.1.2.4.3 The peak at 69 amu shall be set to 100 % relative abundance

5.1.2.4.3.1 Relative to the peak at 69 amu, the peak at 219 amu shall be in the range of 70 % - 250 %.

5.1.2.4.3.2 Relative to the peak at 69 amu, the peak at 502 amu shall be greater than 3 %.

5.1.2.4.3.3 Relative to the peak at 69 amu, the peak at 70 amu shall be in the range of 0.5% -.6 %.

5.1.2.4.4 Relative to the peak at 219 amu, the peak at 220 amu shall be in the range of 3.2 % -5.4 %.

5.1.2.4.5 Relative to the peak at 502 amu, the peak at 503 amu shall be in the range of 7.9 % - 12.3 %.

5.1.2.4.6 M/Z 28 greater than m/z 18 may indicate an air leak somewhere in the system.

5.1.2.4.6.1 If an air leak is detected, the air leak shall be isolated and corrected.

5.1.2.4.6.2 The instrument shall then be tuned again.

5.1.2.5 If any of the above stated parameters are out of specification, the instrument shall be tuned again. If the problem persists, a service engineer shall be contacted or maintenance performed. Once the tune parameters are within specifications, the instrument may be used for casework.

5.1.3 Monthly Py-GC-MS Performance Check

5.1.3.1 To ensure performance, a polyethylene sample shall be analyzed and its Total Ion Chromatogram (TIC) shall be electronically archived. This performance check shall be done at least once a month.

5.1.3.2 If there is a shift in peak retention time by +/-0.3 minute or a change in peak resolution, maintenance shall be performed or a service engineer called. Once maintenance has been performed, a polyethylene sample shall be re-

examined. If the resulting chromatogram is within the limits, the instrument may be used for casework.

5.1.4 Performance Verification for New Instrument Set Up

5.1.4.1 New Py-GC-MS instruments shall be installed by a certified engineer according to the manufacturer's guidelines.

5.1.4.2 The Autotune shall be run on the instrument and checked according to the above criteria.

5.1.4.3 The samples used in the monthly Py-GC-MS quality control check shall be analyzed on the instrument and the resulting chromatographs compared to the same samples acquired on similar instruments. The resulting chromatographs shall have similar peak ratios and component separation in order for the new instrument to be approved for case work.

5.2 Casework Analysis

5.2.1 Samples shall be prepared according to the appropriate technical procedure and shall be transferred to one of the Py-GC-MS operators for analysis.

5.2.2 Once the samples are received, they shall be analyzed using the Pyrolysis and GC-MS methods located in **5.3**.

5.2.3 The resulting TIC shall be included in the Case Record. Additional items such as Extracted Ion Chromatograms (EIC) and Library searches shall be included if performed.

5.2.4 After the method has run, allow the instrument to return to the set program or run a BAKE cycle (ramp internal temperature of oven up to 300 °C) to ensure the column is clean before the next blank is run.

5.3 Py-GC-MS Method Parameters

5.3.1 fbipyro.cds

5.3.1.1 Interface – Rest at 300 °C, max temp of 310 °C.

5.3.1.2 Pyroprobe Clean cycle – 1200 °C for 10.00 S

5.3.1.3 Pyroprobe Blank/Sample Run– Initial temperature at 300 °C at 1.00 S with a ramp of 20.00 mS to 880 °C at 10.00 S.

5.3.1.4 Carrier gas – Helium set between 15-20 mL/min.

5.3.2 PYROLYSIS35MIN.M

5.3.2.1 Injection – Pyroprobe manual injection, helium carries volatilized sample into GC-MS unit through a transfer line that connects to the inlet on the GC-MS.

5.3.2.2 Inlet – Run in split mode at 300 °C with a 50:1 split ratio.

5.3.2.3 Carrier gas – Helium.

5.3.2.4 Oven – Run a temperature program starting at 50.0 °C for 2.00 minutes. Then ramp at 13.0 °C per minute until 300 °C is obtained. Hold at 300 °C for 15.00 minutes.

5.3.2.5 Column – Use a HP-5MS or DB-5MS column which is 0.25 mm in diameter that is approximately 30 m long with a 0.25 µm film thickness. The column will be kept at a constant flow of 0.7 mL/min.

5.3.2.6 Mass spectrometer – The MS Quad temperature is set at 150 °C and the MS source is set at 230 °C. The MS will be run in scan mode using the settings from the atune.u file with an electron multiplier offset of 200 eV. The mass scan range is 34.0 amu to 650.0 amu with a threshold abundance of 150.

5.4 Standards and Controls

5.4.1 There shall be a blank run for each sample in a case.

5.4.1.1 A blank consists of an empty quartz tube (for adhesive-type samples) or an empty quartz tube with a small amount of quartz wool inserted into the bottom (for most other sample types).

5.4.1.2 The blank sample is cleaned (using clean cycle on the pyrolysis software) and is then treated as if it were a sample.

5.4.1.3 The resulting data from the blanks must not have significant peaks that interfere with the analysis.

5.5 Maintenance

5.5.1 The injection port septum shall be changed at least monthly.

5.5.2 The injection port liner shall be changed at least yearly.

5.5.3 The mechanical pump oil shall be changed twice per year.

5.5.4 The septa for the pyrolysis unit nut and probe shall be changed as needed.

5.5.5 The MS source shall be cleaned as needed based on tune acceptance criteria.

5.6 Sampling and Sample Selection – N/A

5.7 Calculations – N/A

5.8 Uncertainty of Measurement – N/A

6.0 Limitations

6.1 Mass spectrometry cannot differentiate between isomers.

6.2 The size and/or the condition of the sample shall determine whether this is an appropriate tool for the analysis.

7.0 Safety

7.1 Burns may result from contact with hot items such as the pyrolysis unit nut, liners, probe, septa nuts, pyrolysis chamber, and transfer line.

7.2 Transfer line needle is sharp and can easily puncture skin. Care shall be exercised when using these items.

8.0 References

8.1 ASTM / SWG Guidelines

ASTM Standard E355, 1996 (2007) "Standard Practice for Gas Chromatography Terms and Relationships." ASTM International, West Conshohocken, PA, 2007.

ASTM Standard E 1610, 2002 (2008), "Standard Guide for Forensic Paint Analysis and Comparison." ASTM International, West Conshohocken, PA, 2008.

Scientific Working Group for Materials Analysis (SWGMAT). "Guideline for the Forensic Examination of Pressure-Sensitive Tapes." Forensic *Science Communications* 2008: 10(4).

8.2 Books / Instrument Manufacturer Materials

Caddy, B., ed. *Forensic Examination of Glass and Paint.* New York: Taylor & Francis, 2001.

Pyrolysis Application Notes. CDS Analytical, Inc. www.cdsanalytical.com

CDS Analytical Inc. Manuals.

Wampler, T.P., ed. *Applied Pyrolysis Handbook.* Boca Raton: CRC Press, 2007.

8.3 Journal Articles

Williams, E.R. and T.O. Munson. "The comparison of black polyvinylchloride (PVC) tapes by pyrolysis gas chromatography." *Journal of Forensic Sciences* 33 (1988): 1163–1170.

8.4 Training Materials

Ryland, S. "Paint Binder Classification by Infrared Spectrometry and Pyrolysis Gas Chromatography." SAFS workshop, Spring 1991.

9.0 Records

- Performance Check and Use Log
- Maintenance Log
- Request for Instrumental Examination of Evidence

10.0 Attachments – N/A

Revision History		
Effective Date	Version Number	Reason
09/17/2012	1	Original ISO Document
02/01/2013	2	Request for Instrumental Examination of Evidence was added as a record.
09/30/2013	3	5.3.2.6 unit regarding threshold was updated
10/18/2013	4	Added issuing authority to header; grammar
08/29/2014	5	Updated header to Physical Evidence Section – Trace Unit, issuing authority to Physical Evidence Section Forensic Scientist Manager. Updated all references in procedure from Trace Evidence Section to Trace Unit 4.2 - Changed aluminum nut to stainless steel