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

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

2.0 Scope – This procedure applies to all gas chromatograph-mass spectrometers set up for liquid samples in the Trace Evidence Section.

3.0 Definitions – N/A

4.0 Equipment, Materials, and Reagents

4.1 Equipment

- Agilent 6890 Gas Chromatograph with Agilent 5973 Mass Selective Detector
- Agilent 7890 Gas Chromatograph with Agilent 5977 Mass Selective Detector
- Hydrogen Generator

4.2 Materials

- Auto sampler vials, 150 µL vial inserts, and crimp seals
- Vial crimper and decrimper
- 2.5 mL airtight syringe
- 10 micro-liter autosampler syringe
- A non-polar capillary column with a (5 %-Phenyl)-methylpolysiloxane stationary phase
- Perfluorotributylamine
- 50 % residual gasoline reference material
- 100 % diesel fuel reference material

4.3 Reagents

- Acetone
- Acetone – Reagent A.C.S. grade
- Carbon disulfide - Reagent A.C.S. grade
- Petroleum ether – Optima Grade
- Helium – UHP

5.0 Procedure

5.1 Start-up and Performance Check

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

5.1.2 Daily GC-MS 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 only needs to be performed once per day. If the instrument is not being used, 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 parameters for passing an Autotune are as follows:

5.1.2.3.1 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.

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

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

5.1.2.3.3.1 Relative to the peak at 69 amu, the peak at 219 amu shall be greater than 40 %.

5.1.2.3.3.2 Relative to the peak at 69 amu, the peak at 502 amu shall be greater than 2.4 %.

5.1.2.3.3.3 Relative to the peak at 69 amu, the peak at 70 amu shall be in the range of 0.5-1.6 %.

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

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

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

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

5.1.2.3.6.2 The instrument shall be tuned again.

5.1.2.4 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 GC-MS Performance Check

5.1.3.1 To ensure performance, the following samples shall be analyzed and the Total Ion Chromatograms (TICs) electronically archived each month the instrument is in use. If the instrument was not in use the previous month, the performance check shall be performed prior to casework.

- Petroleum ether blank

- Carbon disulfide adsorption elution blank
- 50 % residual gasoline reference material
- 100 % diesel fuel reference material

5.1.3.2 If there is a shift in peak retention time by 0.3 minute or more or a change in peak resolution, maintenance shall be performed or a service engineer shall be called. Once maintenance has been performed, the samples shall be re-examined. If the resulting chromatograms are 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 GC-MS instruments shall be installed by a certified engineer according to manufacturer guidelines.

5.1.4.2 The Autotune shall be run on the instrument and checked according to **5.1.2**.

5.1.4.3 The samples used in the monthly GC-MS performance check shall be analyzed on the instrument and the resulting chromatographs are 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 utilized for casework.

5.2 Casework Analysis

5.2.1 Samples shall be prepared for examination according to the appropriate technical procedure.

5.2.2 Once the samples are prepared, they shall be analyzed using one of the GC-MS programs located in the **Attachments**.

5.2.3 Once data has been collected, the resulting data file shall be loaded in the Data Analysis program for examination. At a minimum, the Total Ion chromatograph and Library Search Report shall be included in the case record. Additional items such as Extracted Ion Chromatographs and Library searches shall be included if performed. When a sample is examined by GC-MS only, the Library Search Report is not required for the solvent blank, control blank (charcoal strip) or Performance Check Standard (100% diesel fuel standard).

5.2.4 After the method has run, allow the instrument to return to the set program and leave the GC-MS on.

5.3 Standards and Controls

5.3.1 If the sample was not previously analyzed on the GC-FID, there shall be a minimum of one blank solvent run for each case.

5.3.1.1 If the sample being analyzed is a neat sample, petroleum ether or carbon disulfide shall be used for the blank.

5.3.1.2 If an extraction is performed using acetone, carbon disulfide, petroleum ether, etc., the same solvent shall be used for the blank.

5.3.1.3 If the extraction being performed is a heated headspace extraction, an air blank shall be analyzed.

5.3.2 The resulting data from the blanks shall not have peaks that interfere with the analysis.

5.3.3 The wash bottles on the autosampler shall be filled with acetone or carbon disulfide.

5.4 Maintenance

5.4.1 The septum for the injection port shall be changed at least monthly when in use.

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

5.4.3 The mechanical pump oil shall be changed twice a year.

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

5.5 Sampling – N/A

5.6 Calculations – N/A

5.7 Uncertainty of Measurement – N/A

6.0 Limitations – Mass Spectrometry alone cannot differentiate isomers.

7.0 Safety

7.1 Refer to Appendix A for chemical hygiene and safety precautions for extremely hazardous and particularly hazardous substances.

7.2 Burns may result from contact with hot items such as containers, syringes, liners, and septa nuts.

7.3 Syringe needles are sharp and can easily puncture skin.

7.4 Use extreme caution when dismantling, installing, or transporting compressed gas cylinders. Cylinders shall only be moved with the cylinder cap securely in place.

8.0 References

ATF National Laboratory Center Class. “Laboratory Detection and Identification of Accelerants Found in Arson Debris.”

Saferstein, R. *Forensic Science Handbook.* Volume I. 2nd edition. Upper Saddle River, NJ: Prentice Hall, 2002. Chapter 3: Forensic Applications of Mass Spectrometry, p. 117.

Agilent GC-MSD Chemstation and Instrument Operation Volume 1 G1701DA Version D.00.00 Student Manual. Printed March 2002, Agilent Technologies.

ASTM Guidelines

ASTM Standard E1618, 2006, "Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography–Mass Spectrometry." ASTM International, West Conshohocken, PA, 2006, www.astm.org.

9.0 Records

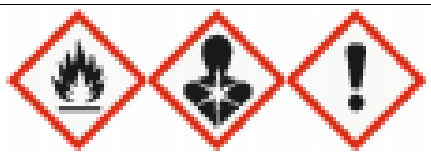
- Maintenance log
- Use log
- Performance Check Chromatographs
- Autotune reports
- Request for Instrumental Examination of Evidence

10.0 Attachments

- Appendix A - Chemical Hygiene and Safety Precautions for Extremely Hazardous and Particularly Hazardous Substances
- Appendix B – Instrument Program Parameters for Agilent 6890 Gas Chromatograph and Agilent 5973 Mass Selective Detector
- Appendix B – Instrument Program Parameters for Agilent 7890 Gas Chromatograph and Agilent 5977 Mass Selective Detector

Revision History		
Effective Date	Version Number	Reason
07/16/2021	10	Added option of carbon disulfide for wash vials to 5.3.3 7.1 – deleted, replaced with new 7.1 7.4 – deleted, replaced with new 7.4 Appendix A - new Appendix C – Retired NSD methods, updated the pre-inject and post-inject solvent washes, updated the flow, removed the statement regarding solvent delay, updated the MS column of the table with a "solvent skip" note

Appendix 1 – Chemical Hygiene and Safety Precautions for Extremely Hazardous and Particularly Hazardous Substances

Gasoline **DANGER: PARTICULARLY HAZARDOUS SUBSTANCE***	
	**HEALTH 2** **FLAMMABILITY 3** **REACTIVITY 0**
Detection of Release	Translucent, straw-colored or light yellow liquid. Strong, characteristic hydrocarbon odor. Sweet-ether like.
Signs/Symptoms of Exposure	• Skin irritation with prolonged or repeated contact. • Eye contact with liquid or vapor may cause irritation. • Ingestion may cause gastrointestinal disturbances, including nausea, vomiting, and diarrhea, and CNS effects similar to alcohol intoxication. In severe cases, tremors, convulsions, loss of consciousness, coma, respiratory arrest, and death may occur. • Inhalation may cause irritation to the nose, throat, lungs, and respiratory tract. CNS effects may include headache, dizziness, loss of balance and coordination, unconsciousness, coma, respiratory failure, and death.
PEL (8-hr TWA)	• Gasoline: 300ppm (ACGIH) • Toluene: 20 ppm (ACGIH), 200 ppm (OSHA); 100ppm (NIOSH) • Butane: 1000 ppm (ACGIH), 800 ppm (OSHA, NIOSH) • Xylenes: 100 ppm (ACGIH, OSHA) • Benzene, 1,2,4 trimethyl: 25ppm (NIOSH) • Ethyl alcohol: 1000 ppm (ACGIH, OSHA, NIOSH) • Ethylbenzene: 20 ppm (ACGIH), 100 ppm (OSHA, NIOSH) • Benzene: 0.5 ppm (ACGIH), 1ppm (OSHA), 0.1 ppm (NIOSH) • Hexane: 50 ppm (ACGIH, NIOSH), 500 ppm (OSHA)
Associated Hazards	Highly flammable liquid and vapor. May cause genetic defects. May cause cancer. May damage fertility or the unborn child. May cause respiratory irritation. May cause drowsiness or dizziness. May be fatal if swallowed and enters airways. Harmful to aquatic life.
Controls	Use adequate ventilation to keep vapor concentrations below exposure and flammability limits. PPE: Gloves – nitrile, neoprene, or PVC are recommended; safety glasses/goggles
Safe handling, storage, disposal	DO NOT SIPHON BY MOUTH. Handle as a flammable liquid. Keep away from heat, sparks, excessive temperature, and open flame! Bond and ground containers during product transfer to reduce the possibility of static-initiated fire or explosion. Use approved vented containers. Keep containers closed and clearly labeled. Empty product containers or vessels may contain explosive vapors. Store in a well-ventilated area. Keep cool.
Emergency Procedures	**Eye Contact:** Immediately flush with clean, low-pressure water for at least 15 min. Hold eyelids open to ensure adequate flushing. Seek medical attention. **Inhalation Exposure:** Remove person to fresh air. If person is not breathing, provide artificial respiration. If necessary, provide additional oxygen once breathing is restored if trained to do so. Seek medical attention immediately. **Ingestion:** DO NOT INDUCE VOMITING. Do not give liquids. Obtain immediate medical attention. If spontaneous vomiting occurs, lean victim forward to reduce the risk of aspiration. Monitor for breathing difficulties. Small amounts of material which enter the mouth should be rinsed out until the taste is dissipated. **Skin Contact:** Remove contaminated clothing. Wash contaminated areas thoroughly with soap and water or with waterless hand cleanser. Obtain medical attention if irritation or redness develops.

	Spills: Small spills: Carefully contain and stop the source of the spill, if safe to do so. Take up with sand or other oil-absorbing materials. Carefully shovel, scoop, or sweep up into a waste container for disposal. Caution, flammable vapors may accumulate in closed containers. Large spills: Evacuate non-essential personnel and remove or secure all ignition sources. Call 911 with hazmat request.

Appendix B

Instrument Program Parameters

Agilent 6890 Gas Chromatograph and Agilent 5973 Mass Selective Detector

Injection – Using the autosampler with a 10 µL syringe injection, perform three pre-injection and three post-injection solvent washes from each wash bottle. Inject the volume of sample indicated below with a fast plunger speed, no sample washes, and 3 sample pumps. The ALCOHOL method uses a manual injection.

Inlet – Run in split mode at 200 °C with the split ratio indicated below.

Carrier Gas – Helium

Column –Use a (5 %-Phenyl)-methylpolysiloxane (such as an HP-5MS) column which is 0.25 mm in diameter that is approximately 30 m long with a 0.25 µm film thickness. The column shall be kept at a constant flow of 0.7 mL/min.

Mass Spectrometer – The transfer line temperature shall be set at 300 °C. The MS Quad temperature is set at 150 °C and the MS source is set at 230 °C. The MS shall be run in scan mode using the settings from the atune.u file with an electron multiplier offset of 0 eV. The mass scan range is 20.0 amu to 400.0 amu with a threshold abundance of 150. Include a solvent delay as indicated below.

Method Name	Injection Volume	Split Ratio	Oven	Mass Spectrometer
ARSONL	0.2 µL	100:1	Run a temperature program starting at 50.0 °C for 2.50 minutes. Then ramp at 9.0 °C per minute until 300 °C is obtained. Hold at 300 °C for 5.00 minutes.	The mass spectrometer shall have a 2.50 minute solvent delay.
ARSON100S	1.0 µL	100:1		
ARSON20S	1.0 µL	20:1		
ARSON2UL20S	2.0 µL	20:1		
ARSONLNSD	0.2 µL	100:1		There is no solvent delay.
ARSON100SNSD	1.0 µL	100:1		
ARSON20SNSD	1.0 µL	20:1		
ALCOHOL	Manual injection of 1 mL using a 2.5 mL airtight syringe.	20:1	Run at an isothermal temperature program set at 80 °C for 15.00 minutes.	There is no solvent delay.

Appendix C

Instrument Program Parameters

Agilent 7890 Gas Chromatograph and Agilent 5977 Mass Selective Detector

Injection – Using the autosampler with a 10 µL syringe injection, perform one pre-injection and five post-injection solvent washes from each wash bottle. Inject the volume of sample indicated below with a fast plunger speed, no sample washes, and 3 sample pumps.

Inlet – Run in split mode at 200 °C with the split ratio indicated below.

Carrier Gas – Hydrogen

Column –Use a (5 %-Phenyl)-methylpolysiloxane (such as an HP-5MS) column which is 0.25 mm in diameter that is approximately 30 m long with a 0.25 µm film thickness. The column shall be kept at a constant flow of 1.2 mL/min.

Mass Spectrometer – The transfer line temperature shall be set at 300 °C. The MS Quad temperature is set at 150 °C and the MS source is set at 230 °C. The MS shall be run in scan mode using the settings from the atune.u file with an electron multiplier offset of 0 eV. The mass scan range is 20.0 amu to 400.0 amu with a threshold abundance of 150.

Method Name	Injection Volume	Split Ratio	Oven	Mass Spectrometer
FIREL	0.2 µL	100:1	Run a temperature program starting at 50.0 °C for 1.50 minutes. Then ramp at 20.0 °C per minute until 300 °C is obtained. Hold at 300 °C for 3.00 minutes.	There is no solvent delay. The MS turns off during the solvent peak.
FIRE100S	1.0 µL	100:1		
FIRE20S	1.0 µL	20:1		
FIRE2UL20S	2.0 µL	20:1		