1. Training Manual for the Analysis of Ignitable Liquids

1.1. Purpose

1.1.1. The Houston Forensic Science Center (HFSC) Trace Analysis Section Ignitable Liquid Analysis Training Manual is designed to develop expert analysts who possess specialized knowledge, skills, and training in the discipline of fire debris examinations.

1.2. Organization of the Training

1.2.1. The training consists of several study segments each covering different aspects of ignitable liquid analysis.

1.2.2. Each study segment contains the following:

1.2.2.1. The Objectives outline the purpose of each study segment.

1.2.2.2. The Core Reading List consists of the reference materials that are required to be read by trainees with no previous experience to successfully complete the study segment. The reading assignments are cumulative; comprehension of prior readings may be required to successfully complete written exercises of subsequent study segments. Note: Readings listed in bold type may need to be acquired by the trainee. If the material cannot be acquired, a substituted reading may be appropriate with trainer's approval.

1.2.2.3. The Supplemental Readings are intended to provide the trainee with additional resources material.

1.2.2.4. The Practical Exercises are designed to provide the trainee first-hand experience with the main concepts of each study segment. The Practical Exercises are located in 1.17 of this manual, with the exception of Study Segment 9, which is comprehensive competency for this training manual. Study Segments 1 – 8 have corresponding practical exercises; however, these may be rearranged or customized for trainees based upon the trainee’s previous experience and needs of the laboratory.

1.2.2.5. The Tests/Discussions may involve combined segments and are located in 1.18 of this manual. Whether written exams are open book, closed book, or a combination of both is intended to be a choice of the trainer. Tests and Discussions may be customized by the trainer for individual trainees based on the trainee’s previous experience.

1.3. Trainee Qualifications

1.3.1. Commencement of the training for ignitable liquid analysis does not assume prior experience in the discipline of fire debris analysis.

1.3.2. It is assumed that the trainee will have a solid understanding of basic organic and inorganic chemistry.

1.3.3. Trainees who do not have previous forensic experience or training must participate in the full training program and must complete the practical exercises portion of each study segment to ensure competency in that area. Trainees who have prior related
training and experience may be able to progress at an accelerated pace. Training may be modified for staff members who have prior related training and/or casework experience.

1.4. Trainee Notebook

1.4.1. The trainee will maintain a notebook throughout the duration of his/her training and will record notes and observations for each study segment. The trainee notebook should be maintained in a neat and current fashion and should be present during conversations with the trainer.

1.5. Completion

1.5.1. In order to successfully complete the training, the trainee must, after completion of all study segments, pass a final competency test, be approved by the Quality Director to conduct analysis for the Division in this discipline, and demonstrate their capability to apply learned knowledge and skills to casework.

1.6. Estimated Time of Completion

1.6.1. The completion time may vary depending on the trainee, operational needs, and time dedicated to this training. The training program should take no longer than one year.

1.7. Acknowledgment

1.7.1. The HFSC Trace Analysis Section thanks the Montana Forensic Services Division Chemical Analysis Unit for its generous use of C-901-A Ignitable Liquid Residue Training, effective 7-16-15, as a model for this training manual.

1.8. STUDY SEGMENT 1: FIRE CHEMISTRY AND INVESTIGATIONS

1.8.1. OBJECTIVES

1.8.1.1. To provide the trainee with a basic understanding of what happens during a fire.

1.8.1.2. To introduce the trainee to current issues in fire scene investigations and to evaluate how the forensic scientist might work with the fire scene investigators on these issues.

1.8.2. Core Reading List


1.8.3. Supplemental Readings
1.8.3.2. ATF Basic Fire Debris Analysis Course June 10-13, 2002, Athens Ohio, Sections 1 and 2.

1.9. STUDY SEGMENT 2: PROPERTIES OF IGNITABLE LIQUIDS

1.9.1. OBJECTIVES
1.9.1.1. To provide the trainee with a basic understanding of the oil refining process.
1.9.1.2. To introduce the trainee to the various types of ignitable liquids currently available on the commercial market.

1.9.2. Core Reading List

1.9.3. Supplemental Readings
1.9.3.1. Kerosene and Jet Fuel, Chemical and Physical Properties
1.9.3.2. Fuel Oil (Heating Oil), Chemical and Physical Properties

1.9.3.3. “A Basic Overview of a Petroleum Refinery”, unknown source, available in the online Trace Analysis Ignitable Liquid Reference Library.

1.10. STUDY SEGMENT 3: INSTRUMENTATION

1.10.1. OBJECTIVES

1.10.1.1. To develop an understanding of how the GC and GC-MS are used in ignitable liquid residue analysis.

1.10.1.2. To develop an understanding of the strengths and weakness associated with the GC and GC-MS.

1.10.1.3. To demonstrate the use of the GC and GC-MS.

1.10.2. Core Reading List


1.10.2.6. “GC/MS Analysis of Fire Debris Extracts,” Section 5, NFSTC Advanced Arson School, Student Manual (1996)


1.10.3. Supplemental Readings


1.11. STUDY SEGMENT 4: SAMPLE COLLECTION AND EXTRACTIONS

1.11.1. OBJECTIVES

1.11.1.1. To develop an understanding of the methods and techniques that are available for the analysis of ignitable liquids.

1.11.1.2. To develop an understanding of the strengths and weaknesses associated with the different extraction methods available for ignitable liquid residue analysis.

1.11.1.3. To demonstrate the different extraction technologies, including heated headspace, passive adsorption/elution, and solvent extractions.

1.11.1.4. To develop an understanding of the evidence collection, handling, and packaging of fire debris analysis.

1.11.2. Core Reading List


1.11.2.2. ASTM E1386, “Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Solvent Extraction”

1.11.2.3. ASTM E1388, “Standard Practice for Sampling of Headspace Vapors from Fire Debris Samples”

1.11.2.4. ASTM E1412, “Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Activated Charcoal”


1.11.3. Supplemental Readings


1.11.3.4. Newman, R. T., “An Evaluation of Multiple Extractions of Fire Debris by Passive Diffusion,” Pinellas County Forensic Laboratory, FL, and available in the online Trace Analysis Ignitable Liquid Reference Library.

1.12. STUDY SEGMENT 5: INTERPRETATIONS

1.12.1. OBJECTIVES

1.12.1.1. To develop an understanding of the Ignitable Liquid Classification System as defined in ASTM E1618.

1.12.1.2. To demonstrate the ability to differentiate ignitable liquids into the appropriate classes of the Ignitable Liquid Classification System.

1.12.2. REQUIRED READING


1.12.3. Supplemental Readings
- 1.12.3.2. ASTM E1387, “Standard Test Method for Flammable or Combustible Liquid Residues in Extracts from Samples of Fire Debris by Gas Chromatography”

1.13. STUDY SEGMENT 6: PROBLEMATIC SAMPLES

1.13.1. OBJECTIVES
- 1.13.1.1. To introduce the trainee to some of the sample matrices that can cause interference with chromatographic data.
- 1.13.1.2. To help the trainee develop the ability to recognize chromatographic patterns that may be caused by pyrolysis products.
- 1.13.1.3. To demonstrate pyrolysis, turpentine, and microbial degradation chromatographic patterns.

1.13.2. Core Reading List

1.13.3. Supplemental Readings

1.14. STUDY SEGMENT 7: COMPARISONS

1.14.1. OBJECTIVES

1.14.1.1. To introduce the trainee to the methods and procedures that can be used to compare gasoline samples.

1.14.1.2. To recognize the limitations of ignitable liquid comparisons.

1.14.1.3. To demonstrate the ability to differentiate between automotive gasoline samples.

1.14.2. Core Reading List


1.14.3. Supplemental Readings


1.15. STUDY SEGMENT 8: DOCUMENTATION AND TESTIMONY

1.15.1. OBJECTIVES

1.15.1.1. To introduce the trainee to logbooks, notes, and other paperwork necessary to properly document the analysis of fire debris.

1.15.1.2. To prepare the trainee for the formal courtroom presentation of fire debris analysis.

1.15.2. Core Reading List


1.15.3. Supplemental Readings

1.16. STUDY SEGMENT 9: Competency Examination

1.16.1. OBJECTIVES
1.16.1.1. To instill self-confidence in the analytical ability of the trainee.
1.16.1.2. To ensure that the trainee has acquired specialized knowledge, skills, and abilities in the discipline of fire debris examinations.
1.16.1.3. To ensure appropriate documentation and report writing skills.
1.16.1.4. To ensure appropriate techniques and confidence for court presentation.

1.16.2. STUDY/DISCUSSION EXERCISES
1.16.2.1. Discuss the results of the competency evaluation (see practical exercises) with the instructor.
1.16.2.2. Evaluate the Course of Study and provide recommendations for future revisions.

1.16.3. PRACTICAL EXERCISES
1.16.3.1. Process the practical competency (mock case) provided by your trainer. Analyze and issue a report for each case as if it were actual casework.
1.16.3.2. Undergo a mock trial on the analysis of fire debris.
1.16.3.3. If exams were not administered with each section, complete the Section’s written test on fire debris analysis.

1.17. PRACTICAL EXERCISES
1.17.1. Practical Exercises Corresponding to Study Segment 1
1.17.1.1. Demonstrate the flammability of the vapor above the surface of an ignitable liquid versus the flammability of the liquid itself.
1.17.1.2. Analyze pyrolysis products found in a variety of carpeting.
1.17.1.3. If possible, observe a canine as they conduct a search for ignitable liquids.

1.17.2. Practical Exercises Corresponding to Study Segment 2
1.17.2.1. Examine the different standard chromatograms that have been run in the different classes as defined by ASTM E1618. Observe the differences and similarities that are present.
1.17.2.2. Visit a hardware store or a home center and observe the numerous types of solvents and other ignitable liquid products that are available today. The trainee must document their observations.
1.17.2.3. Analyze various ignitable liquid products found in hardware stores or a home center.

1.17.3. Practical Exercises Corresponding to Section 3
1.17.3.1. Run an autotune and evaluate the results with your trainer.
1.17.3.2. Demonstrate your ability to manually produce an extracted ion chromatogram.
1.17.3.3. Set up and run a sequence on the GC-MS utilizing lab macros. The sequence should include samples from all categories of ASTM E1618.
1.17.3.4. Demonstrate the maintenance of the GC-MS injection port and detector.

1.17.3.5. Dilute or dissolve the following and run on the GC-MS:
   - paraffin wax
   - motor oil
   - petroleum jelly

1.17.3.6. Analyze the following by GC-MS headspace:
   - methanol
   - lacquer thinner
   - diesel

1.17.4. Practical Exercises Corresponding to Section 4

1.17.4.1. Explain different areas of possible evidence collection of ignitable liquid residue at fire scenes.

1.17.4.2. Explain and/or demonstrate when fire debris evidence must be repackaged in the laboratory.

1.17.4.3. Demonstrate proper evidence packaging for liquids, cans, bags, and sample charcoal strips.

1.17.4.4. Analyze the following samples via room temperature passive headspace extraction by active charcoal on the GC-MS:
   - Ronson lighter fluid at 10 µL, 50 µL and 500 µL
   - Mineral spirits at 10 µL, 50 µL, and 500 µL
   - Unweathered gasoline at 10 µL, 50 µL, and 500 µL
   - Diesel at 10 µL, 50 µL, and 500 µL

1.17.4.5. Repeat analyses for 1.17.4.4. (50 µL samples only) above by elevating the temperature to 80 degrees for 30 minutes and analyzing on the GC-MS.

1.17.4.6. Analyze the samples in 17.4.4. (50 µL samples only) via passive headspace extraction by active charcoal at 80 degrees for 1 hour and run on the GC-MS.

1.17.4.7. Analyze the samples in 17.4.4. (50 µL samples only) via passive headspace extraction by active charcoal at 60 degrees for overnight and run on the GC.

1.17.4.8. Take some charred fire debris and spike it with 100 µL of 50% weathered gasoline. Extract with pentane. Concentrate the solvent to approximately 1 ml and analyze by GC-MS.

1.17.4.9. Analyze the samples in 17.4.4. (50 µL samples only) via passive headspace extraction by active charcoal degrees for 1 hour using a charcoal strip that is ½ the normal size.

1.17.4.10. Analyze the samples in 17.4. (50 µL samples only) via passive headspace extraction by active charcoal at 80 degrees for 1 hour using a charcoal strip that is 4 times normal size.
1.17.4.11. Add 50 µL of 50% weathered gasoline to a pint, quart, and gallon sized cans containing Kimwipe®. Analyze by passive charcoal adsorption/elution and GC-MS. Compare the results.

1.17.4.12. Add 50µL of 50% weathered gasoline to a quart can. Analyze by passive charcoal adsorption/elution and GC-MS. Repeat until no longer able to see gasoline pattern on chromatogram. Use cloth as a sample substrate.

1.17.5. Practical Exercises Corresponding to Section 5

1.17.5.1. Weather a gasoline sample to 50%, 75%, 90%, and 99%. Run on GC-MS. Discuss results with trainer.

1.17.5.2. Run mixtures of the following on the GC-MS:
- gasoline and diesel
- LPD and MPD
- Isopar and MPD

1.17.5.3. Analyze the following samples by GC-MS:
- Gasoline by headspace
- Gasoline after dilution in a solvent
- Gasoline after an adsorption/elution on a charcoal strip
- Gasoline after solvent extraction on fire debris.

- Repeat steps above on diesel.
- Repeat steps above on a pyrolyzed piece of polyethylene.

1.17.5.4. Take the samples provided by your trainer and analyze by passive headspace extraction by active charcoal at 80 degrees for 1 hour. The trainee should conduct testing as necessary to complete the analysis and classify each sample.

1.17.5.5. Take the chromatograms provided by your trainer and classify each.

1.17.5.6. Run and compare a sample of an isopar and a similar naphthenic-paraffinic compound. Note the similarities and differences.

1.17.6. Practical Exercises Corresponding to Section 6

1.17.6.1. Analyze samples of turpentine and different wood types. Compare the results.

1.17.6.2. Analyze samples of diesel, burned roofing material, and burned polyethylene. Compare the results.

1.17.6.3. Develop an experiment that will show how gasoline can be selectively degraded by microbial degradation in a rich organic soil over time. Also show how freezing will inhibit this degradation.

1.17.6.4. Pyrolyze numerous possible substrates and other common household items. Extract by charcoal absorption/elution and analyze on the GC-MS. The samples should include a variety of materials likely to be seen in casework. A partial list would include: various carpets, carpet pads, different woods, laminate flooring from different manufacturers, plastic, asphalt shingles, linoleum, shoes and other clothing.
The trainer will review substrates analyzed to determine if the number and type of samples examined is adequate. Samples should be examined burned and unburned.

1.17.7. Practical Exercises Corresponding to Section 7
1.17.7.1. Analyze several samples of automotive gasoline by GC-MS. Compare the results.
1.17.7.2. Weather at least two gasoline samples (three if available) approximately 25%, 50%, 75%, and 90%. Compare the results with the original liquid and with each other. Also compare with other gasoline samples available. Use the GC-MS for the analyses.
1.17.7.3. Examine the chromatograms that have been provided by your trainer. Attempt to match the question samples back to known standards.

1.17.8. Practical Exercises Corresponding to Section 8
1.17.8.1. Develop a Curriculum Vitae/SOQ with updated qualifications.
1.17.8.2. Review at least 5 fire debris reports as if the trainee were the technical reviewer.
1.17.8.3. Analyze a sample provided by your trainer. Write a report on the results of this analysis.
1.17.8.4. Observe court testimony provided by other staff members.

1.18. TEST/DISCUSSION EXERCISES
1.18.1. Corresponds to Segment 1
1.18.1.1. What is flash point? What are the flash points of the following compounds: automotive gasoline, kerosene, paint thinner, methanol and diesel?
1.18.1.2. What is the fire tetrahedron? Name the four corners of the tetrahedron.
1.18.1.3. What is pyrolysis? Why is it important to the forensic analyst?
1.18.1.4. Why do we use the term ignitable liquid rather than accelerant?
1.18.1.5. What is fire? Smoke? Octane number? Explosive limits?
1.18.1.6. What significance is depth of char at a fire scene? What are some of the misconceptions about char?
1.18.1.7. What significance does spalling have at a fire scene? What are some of the misconceptions about spalling?
1.18.1.8. What compounds are canines usually trained with? What specific chemicals in these compounds do the dogs recognize?

1.18.2. Corresponds to Study Segment 2
1.18.2.1. What is the difference between a distillate and a straight run product?
1.18.2.2. When do we see oxygenated gasoline and why?
1.18.2.3. What is reformulated gasoline? Would it be chromatographically different than un-reformulated gasoline?
1.18.2.4. What is the difference between kerosene and jet fuel?
1.18.2.5. Why are there so many types of aviation fuels?
1.18.2.6. Discuss what the lab requirements are for an ignitable liquid standard.
1.18.2.7. Discuss why the same formulation is often times labeled differently.

1.18.3. Corresponds to Study Segment 3
1.18.3.1. Discuss and demonstrate the usage of the GC-MS for ignitable liquid analysis.
1.18.3.2. Discuss the requirements of a mass spectral match. Discuss retention time variation.
1.18.3.3. What is an autotune and why is it important? What compound is used for the autotune? What ions are prominent in the autotune spectrum?
1.18.3.4. What is the difference between split and splitless injection in a GC? Which one do we use for ignitable liquid analysis and why?
1.18.3.5. Define the following terms:
   • Ion source
   • Base peak
   • Relative abundance
   • Isotope
   • Extraction ion profile
   • Target compounds
1.18.3.6. List the sources of potential contamination and/or decreasing sensitivity in the GC injection port.
1.18.3.7. What are the functions of the foreline pump and the diffusion pump in the MS?
1.18.3.8. On an autotune report, ions at masses 18, 28 and 32 are present in abundance of roughly 50% of the 131 peak. What is the likely cause of these ions?
1.18.3.9. Is the molecular ion always present in the mass spectrum? Why or why not?
1.18.3.10. Why do we normally not identify every peak in an ignitable liquid chromatogram?
1.18.3.11. What ions do we use to profile alkanes, cycloalkanes, aromatics, naphthalenes, terpenes, styrenes and alcohols?
1.18.3.12. Discuss the use of the GC versus the GC-MS. Is the GC-MS necessary for all identifications?
1.18.3.13. Discuss the differences between a total ion chromatogram, an extracted ion chromatogram and a target compound chromatogram.

1.18.4. Corresponds to Study Segment 4
1.18.4.1. Discuss the usage of charcoal adsorption/elution, headspace, solvent extraction and SPME.
1.18.4.2. What type of samples work best with each of the four extraction types listed in question #1?
1.18.4.3. What are the advantages and disadvantages of each of the four extraction types listed in question #1?
1.18.4.4. How would temperature affect the chromatographic data in headspace and charcoal adsorption/elution techniques?
1.18.4.5. How does sample concentration affect the chromatographic data in headspace and charcoal adsorption/elution techniques?
1.18.4.6. What other adsorbents can be used to trap ignitable liquid residues in adsorption/elution techniques?

1.18.4.7. Is charcoal a good adsorbent for alcohol? For hydrocarbons?

1.18.4.8. What solvents can be used for ignitable liquid solvent extractions?

1.18.5. Corresponds to Study Segment 5

1.18.5.1. Discuss the criteria for each of the classes as defined in the Ignitable Liquid Classification Systems used in the ASTM procedures.

1.18.5.2. How is fuel oil defined in the ASTM procedures?

1.18.5.3. How often should the test mixture be analyzed?

1.18.5.4. Discuss what criteria you would use to differentiate an isopar from a naphthenic-paraffinic class compound?

1.18.5.5. What are the minimum requirements needed to place a compound into the gasoline range?

1.18.5.6. How does weathering affect our ability to classify a compound into its original class?

1.18.5.7. What are the two branched alkanes that are present in petroleum products?

1.18.5.8. What are the report requirements per the ASTM procedures?

1.18.5.9. What extraction technique is usually required if a sample is to be classified as kerosene or a HPD?

1.18.6. SEGMENT 6

1.18.6.1. What are some of the common chemical components that are present in both ignitable liquid samples and pyrolysis products?

1.18.6.2. What can be done to reduce the amount of pyrolysis products present in casework samples? What can the fire scene investigator do to help the laboratory determine if pyrolysis products are interfering with the analysis of fire debris?

1.18.6.3. What chemical component found in “environmentally safe” cleaners has a mass spectrum that is related to terpenes?

1.18.6.4. What extraction ions do we use to monitor for terpenes? What structure relates to these ions?

1.18.6.5. How can diesel be differentiated from asphalt condensation products? From burned polyethylene?

1.18.6.6. What components of an ignitable liquid can be degraded by soil microbes?

1.18.6.7. Does microbial degradation occur in all types of soil? Why or why not?

1.18.6.8. How can microbial degradation be controlled in casework samples?

1.18.7. Corresponds to Study Segment 7

1.18.7.1. What are the some of the problems with comparing automotive gasoline that has been recovered from fire debris with a liquid sample?

1.18.7.2. Can other ignitable liquids be compared besides automotive gasoline? Why or why not?
1.18.7.3. What characteristics allow for automotive gasoline comparisons?
1.18.7.4. What conclusions can be derived from automotive gasoline dye analysis?
1.18.7.5. What other components (besides hydrocarbons) can be compared in automotive gasoline?

1.18.8. Corresponds to Study Segment 8
   1.18.8.1. Discuss appropriate court demeanor and dress.
   1.18.8.2. What is the difference between a lay witness and an expert witness?
   1.18.8.3. When you are delivering testimony and one of the attorneys says “Objection”, what do you do?
   1.18.8.4. Explain fire debris analysis as you would in court.
   1.18.8.5. In a jury trial, whom should the witness address?
   1.18.8.6. What information should be included in your notes?
   1.18.8.7. What logbooks do we maintain related to fire debris analysis?
   1.18.8.8. What information should be included in a report?