Washington State Patrol

Crime Laboratory Division

Materials Analysis
Ignitable Liquids, Residues, and Products Training Manual

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1 INTRODUCTION

1.1 PURPOSE

This manual contains an outline for training and/or assessing a forensic scientist in the area of ignitable liquids (IL), ignitable liquid residues (ILR), and other ignitable products analysis. The various study segments should be covered in the order presented.

This manual endeavors to promote and maintain consistency and quality among forensic scientists performing ignitable liquid analyses across the Crime Laboratory Division. Certain inherent aspects of IL analysis prohibit the establishment of a rigid set of standard procedures to cover every case. Sufficient latitude should be given to allow for independent thought and individual freedom in selecting alternative courses of action. Upon completion of this training program, the trainee will be thoroughly familiar with the options available to perform an examination of most types of evidence that may be received.

1.2 EXPECTATIONS

The trainee is expected to have successfully completed the following study segments from the Primary Foundation: Basic Practical Microscopy, Gas Chromatography, Infrared Spectroscopy, Mass Spectrometry.

Trainees who have prior related training and experience may be able to progress through the training program at an accelerated pace or skip certain study segments. The required documentation of such related training and/or experience will be left to the technical lead(s) or their designee.

The instructor must be experienced in the area of IL analysis. The instructor's casework and courtroom experiences, both prior and present, provide a unique aspect to the trainee's learning process that is impossible to duplicate in this training program. The instructor will share such experiences with the trainee. Although the trainee's primary interaction will be with the assigned instructor, this program promotes and encourages discussions with other experienced examiners.

The trainee will maintain a notebook or multiple notebooks throughout the duration of this training program 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. Upon completion of training, the trainee will maintain the training notebook for the duration of their career.

The trainee should be continuously evaluated throughout the training for comprehension and competency in theoretical knowledge, basic practical skills, and critical thinking skills. Training is progressive and continuously builds on and reinforces prior learning. Deficiencies on any of the training steps may occur during the course of the training and should be rectified. It is important that these deficiencies be openly and promptly discussed among the trainee, trainer, technical lead, and/or supervisor, as appropriate. Repeating training steps and testing may be necessary to satisfactorily complete this training program.

In order to successfully complete this training program the trainee must successfully complete a closed book written exam passed with 80% and successfully complete a competency exam passed with a 100%. The written examination may be comprehensive or dispersed throughout the training program. A mock trial will be completed following the successful completion of the competency examination. The completion of these steps will be documented on a training checklist located at the end of this manual. The trainer is responsible for writing an interoffice communication (IOC) to the trainee's supervisor recommending the trainee commence supervised casework when the trainee has successfully completed all segments of the Ignitable Liquids, Residues, and Products Training Manual. Upon approval the trainee will complete supervised casework. Following successful completion of supervised casework, the trainer or trainee's supervisor will write an IOC recommending the trainee be authorized for independent casework and technical review of ignitable liquids, residues and products casework. The trainee's supervisor will maintain copies of training IOCs and authorizations in their files.

1.3 ORGANIZATION OF THE TRAINING MANUAL

This training manual consists of several study segments, each covering different aspects of IL analysis. The study segments are organized in a specific manner to build on each other. Understanding fire chemistry, dynamics, scene investigation, and legal issues surrounding fire are foundational to the analytical process and will be covered in the first segment of training. Sources and classification of ignitable liquids are covered in the second training segment. Preservation and packaging of volatile evidence and comparison control samples are covered in the third phase of this training program. ILR recovery methods and ignition testing will be covered in the fourth segment. Segment five will introduce the trainee to data generation using gas chromatography-mass spectrometry. Interferences and data interpretation are covered in section six of the training. The final segment will cover incendiary devices, unusual evidence, and special situations.

Each study segment is comprised of six sections:

Objectives – Summarizes the purpose of each study segment.

Topic Areas – Designates topics to be included in the study segment.

Critical Terms – Lists of terms and phrases which will be defined and understood in the study segment.

Reading and References – Lists the reference materials that should be utilized to complete the study questions and practical exercises. The trainer will suggest which materials should be read in their entirety and which references should be used for general knowledge.

Study Questions – Lists questions that assist the trainee in comprehension of the readings, promotes active discussion between the trainer and trainee, and documents understanding of the topic areas. Written answers to these questions will be maintained in the training notebook as documentation of training.

Practical Exercises – Hands on activities that are designed to provide the trainee first-hand experience with the main concepts of each study segment. Data or written explanation for each exercise must be maintained in the training notebooks.

1.4 SAFETY

The trainee should have an understanding of the hazards associated with the solvents and compounds of interest in ignitable liquid residue analysis. Evidence related to this type of casework often contains broken glass, jagged pieces of metal and wood, and other sharp materials. Cans containing concentrated volatiles may be under pressure and expel some of their contents when opened. Evidence should be processed in a fume hood whenever possible.

Ignition testing and burning/pyrolyzing comparison samples should be performed in a functioning fume hood. The flame should be completely extinguished and the glass wool and vessel cooled completely before disposal.

2 OVERVIEW OF FIRE – CHEMISTRY, DYNAMICS, AND INVESTIGATION OF THE SCENE

2.1 OBJECTIVES

1. To familiarize the student with the basic terms used to describe the chemistry of fire and the basic considerations of fire investigation that relate to analysis.
2. To provide the student with an overview of fire chemistry and behavior.
3. To give the student a basic understanding of fire scene investigation and the role filled by the forensic scientist.

2.2 TOPIC AREAS

1. Fire Chemistry and Dynamics
    a. Combustion Chemistry
    b. Properties of Ignitable Liquids
    c. Ignition Sources
    d. Effects of heat and fire
    e. Effects of evaporation and combustion of ignitable liquids
    f. Pyrolysis processes of fuels
    g. Thermal degradation products from ordinary combustibles
        i. physical products
        ii. chemical products
    h. Fire Suppression
2. Fire Investigation
    a. Scene preservation and contamination
    b. Identification of origin
    c. Identification of ignition sources
    d. Application of the scientific method to the fire investigative process
    e. Establishment of cause
    f. Selection of laboratory samples and comparison samples
    g. Recovery and packaging (See also Section 3)
    h. Investigator's expectations of forensic analysis
        i. identification of product
        ii. unique source identification

2.3 CRITICAL TERMS

1. Accelerant
2. Arson (and related legal definitions)
3. Reckless Burning (and related legal definitions)
4. Auto Ignition Temperature
5. Combustible Liquid

6. Conduction
7. Convection
8. Deflagration
9. Detonation
10. Direct Flame Impingement
11. Fire
12. Fire Cause
13. Fire Tetrahedron
14. Flammable Limit
15. Flammable Liquid
16. Flash Point
17. Flame Point
18. Flaming Fire
19. Glowing Fire
20. Ignitable Liquid
21. Ignition
22. Motive
23. Point of Origin
24. Pyrolysis
25. Radiation
26. Ignition Temperature
27. Spontaneous Ignition
28. Lower Explosive Limit
29. Upper Explosive Limit
30. Vapor Density

2.4 READING AND REFERENCES

Almirall J, Furton K, eds. **Analysis and Interpretation of Fire Scene Evidence**. Boca Raton: CRC Press. 2004.

Babrauskas V. **Ignition Handbook**. Issaquah, WA: Fire Science Publishers. 2003.

Byron D. **The effects of surfactants and microbes on the identification of ignitable liquids in fire debris analysis.** Fire and Arson Investigator. 2002; 53(1):50.

Cote A, Linville J. NFPA **Fire Protection Handbook.** Quincy, MA: NFPA. current edition.

Daeid NN, ed. **Fire Investigation.** Boca Raton: CRC Press. 2004.

DeHaan J. **Kirk's Fire Investigation.** Upper Saddle River, New Jersey: Prentice Hall. current edition.

Drysdale, Douglas. **An Introduction to Fire Dynamics.** Wiley & Sons, 3rd Edition. 2011.

Faraday M. **The Chemical History of a Candle.** Mineola, New York: Dover Publications. 2002.

Lang T, Dixon BM. **The possible contamination of fire scenes by the use of positive pressure ventilation fans.** Canadian Society of Forensic Sciences Journal. 2000; 33(2):55-60.

Lentini JJ, Smith DM, and Henderson RW. **Baseline characteristics of residential structures which have burned to completion: The Oakland experience.** Fire Technology. August 1992; 28.

Lentini, JJ. **Scientific Protocols for Fire Investigation.** CRC Press, 2nd Edition. 2012.

Mahoney E. **Fire Suppression Practices and Procedures.** Englewood Cliffs, NJ: Brady Publishing. current edition.

Midkiff CR. **Arson and explosive investigation**. in: Saferstein, R, ed. Forensic Science Handbook, Vol. I. Upper Saddle River, New Jersey: Prentice-Hall. current edition.

National Fire Protection Association. **NFPA 921: Guide for Fire and Explosion Investigations**. Quincy, Massachusetts: NFPA. current edition.

RCW Chapter 9A.48. Arson, Reckless Burning, and Malicious Mischief. Available at: http://apps.leg.wa.gov/RCW/default.aspx?cite=9A.48.

Stauffer E. **Concepts of pyrolysis for fire debris analysts.** Science and Justice. 2003; 43(1):29-40.

Stauffer, E., Dolan, J., Newman, R., **Fire Debris Analysis.** Academic Press. 2008.

Technical Working Group on Fire/Arson Scene Investigation. **Fire and Arson Scene Evidence: A Guide for Public Safety Personnel.** Washington, DC: National Institute of Justice; 2000.

2.5 STUDY QUESTIONS

1. What factors are needed for a fire to start? What is needed for a fire to progress?
2. Describe how fire occurs, progresses and behaves.
3. What happens to an ignitable liquid when it is exposed to a fire?
4. What are the fire investigator's goals at a fire scene? How does the fire investigator proceed during an investigation? What steps are taken?
5. How should samples be collected from a fire scene? How should they be stored? Why?
6. What are the fire investigator's expectations of and needs of the laboratory? When can and can't those expectations or needs be met?

2.6 PRACTICAL EXERCISES

There are no practical exercises for this segment of training.

3 SOURCES AND CLASSIFICATIONS OF IGNITABLE LIQUIDS

3.1 OBJECTIVES

1. Demonstrate a basic understanding of the process of refining petroleum products from crude oil.
2. Describe the chemical conversion processes of cracking, alkylation, reformation, and others, used to increase yield and improve specifications of fuel and specialty products.
3. Understand the importance of chemical composition of petroleum products in the classification and identification of ignitable liquids.
4. Understand the relationship between carbon number(s) in homologous series and physical properties.
5. Describe the main chemical groups of hydrocarbons and oxygenates.
6. Understand the difference between petroleum products and petroleum distillates.
7. To understand the sources and types of ignitable liquids not derived from petroleum.

3.2 TOPIC AREAS

1. Refinery Processes
    a. Crude Oil Sources and Composition
    b. Refining Processes
    c. Relating Refinery Fractions to Commercially Available Products
    d. Distribution
    e. Obtaining Specific Product Information
2. Petroleum Products
    a. Alkanes
    b. Aromatics
    c. Cycloalkanes
    d. Alkenes
    e. Alkynes
    f. Indanes/Indenes
    g. Oxygenates
    h. Light, Medium and Heavy Petroleum Products
    i. Miscellaneous Products
3. Non-Petroleum Products
    a. Sources of non-petroleum ignitable liquids
    b. Uses of non-petroleum ignitable liquids
    c. Considerations affecting analysis
4. Classification of Ignitable Liquids
    a. Gasoline
    b. Petroleum distillates

c. Isopariffinic products
d. Aromatic products
e. Naphthenic paraffinic products
f. Normal alkane products
g. De-aromatized distillates
h. Oxygenated solvents
i. Miscellaneous

3.3 CRITICAL TERMS

1. Petroleum Product Refining From Crude Oil
2. Petroleum Tower Distillation
3. Petroleum Catalytic Cracking
4. Petroleum Catalytic Reforming
5. “Gasoline” (Both as a created product and as a product classification)
6. Distillate
7. Isoparaffinic Products
8. Aromatic Products
9. Naphthenic-Paraffinic Products
10. Normal Alkane Products
11. De-aromatized Distillates
12. Oxygenated Solvents
13. “Miscellaneous” Products
14. Turpentine
15. Classifications of Ignitable Liquids

3.4 READINGS AND REFERENCES

Refinery Processes

Fuel from Crude. Available at: http://www.petroleum.co.uk/refining

Gasoline and Other Motor Fuels. Encyclopedia of Chemistry and Technology. Vol. 10. 2nd Ed. 1982: 463-498.

How It Works – The Refining Process. Availabile at: http://www.refiningnz.com/visitors--learning/classroom--learning-resources/learning-centre.aspx

Oil: Crude and Petroleum Products Explained. Available at: https://www.eia.gov/energyexplained/index.cfm?page=oil_refining

Thornton JI, Fukiyama B. **The Implications of Refining Operations to the Characterization and Analysis of Arson Accelerants.** Arson Analysis Newsletter. Part I. Physical Separation, pages 1-16, May 1979; Part II. Chemical Conversions, Treating Processes, and Subsidiary Processes, pages 1-16, August 1979.

Petroleum Products

Black Gold: The Story of Oil (part of the Empires of American Industry Series Video) – The History Channel.

Composition and Refining of Petroleum, infoplease, http://www.infoplease.com/ce6/sci/A0860338.html, 2004.

DeHaan JD. **Our changing world. Part 1: furnishings.** Fire and Arson Investigator. 2002;16-17.

Leffler WL. **Petroleum Refining in Non-Technical Language.** 3rd Ed. Tulsa: PennWell Corporation; 2000.

Petroleum, Wikipedia encyclopedia, http://en.wikipedia.org/wiki/Petroleum

Potter T, Simmons, K. **Volume 2: Composition of Petroleum Mixtures.** Amherst Scientific Publishing. 1998.

Speight, JG. **Handbook of Petroleum Analysis.** John Wiley & Sons Inc. 2001.

Speight JG, Ozum B. **Petroleum Refining Processes.** New York: Marcel Dekker Inc. 2002.

Speight, JG. **The Chemistry and Technology of Petroleum.** Chemical Industries. Vol. 76. New York: Marcel Dekker Incorporated. 1999.

Non-Petroleum Products

Trimpe MA. **Turpentine in Arson Analysis.** J Forensic Sci. 1991;36:1059-1073.

Classification of Ignitable Liquids

ASTM E1618, **Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry,** current edition.

Ignitable Liquids Database. Available at: http://ilrc.ucf.edu/index.php

Newman R. **Forensic Fire Debris Analysis in Forensic Chemistry:Fundamentals and Applications.** John Wiley & Sons, Ltd. 2015.

Peschier LJC, Gutters MMP, Hendriske JN. **Using Alkylate Components for Classifying Gasoline in Fire Debris Samples.** J Forensic Sci. 2017 May 39. doi:10.1111/1556-4029.13563. PubMed PMID: 25886928.

Stauffer E, Dolan J, Newman R, **Fire Debris Analysis**. Academic Press. 2008.

3.5 STUDY QUESTIONS

1. What is the purpose of desalting?
2. What is the purpose of alkylation?
3. List the 6 primary straight run products which result from fractional distillation of crude oil. For 3 of these, list 3 common commercially available products.
4. Explain octane numbers.
5. List 5 major compounds in gasoline.
6. Discuss petroleum production from crude oil to products.
7. Discuss the uses of petroleum products based on their characteristics and properties.
8. List the eight classes of ignitable liquids using the ASTM 1618 Ignitable Liquids Classification scheme. Give several examples of products which may be included in each sub-class.

3.6 PRACTICAL EXERCISES

1. If possible, arrange a tour of an oil refinery.
2. Classify at least thirty different samples provided by the trainer. Document the characteristics that support the classification for each sample. This practical exercise will be completed to the satisfaction of the instructor.

4 PACKAGING AND PRESERVING OF EVIDENCE, COMPARISON SAMPLES, & SAMPLING MATERIALS

4.1 OBJECTIVES

1. Demonstrate an understanding of evidence collection.
2. Demonstrate knowledge of correct documentation and packaging of evidence.
3. Demonstrate correct evidence preservation techniques.
4. Demonstrate correct procedures to establish valid chain of custody.
5. Demonstrate an understanding of the need for comparison samples in fire debris cases.
6. Demonstrate the best sources for comparison samples in specific situations.
7. Demonstrate an understanding of absorbent materials effective for collecting ignitable liquid residues from non-removable, porous matrices.

4.2 TOPIC AREAS

1. Documentation of evidence
    a. Scene
    b. Laboratory
        i. Date/time of examination
        ii. Description of evidence packaging
        iii. Preliminary description of evidence
            1. Odor
            2. General evaluation of contents
        iv. Post-analysis description of evidence
2. Preservation of evidence
    a. Types of packaging
        i. Cans
            1. Lined
            2. Unlined
        ii. Glass jars
        iii. Nylon, polyethylene or other vapor-tight fire debris bag
        iv. Paper or zip-lock type plastic bags
    b. Refrigeration
    c. Freezing
        i. Microbial degradation
    d. Protection
        i. Sunlight
        ii. Heat
        iii. Breakage (glass containers)

e. Time
    i. Shelf Life
    ii. Visual Inspection

3. Chain of Custody
    a. Intact
    b. Legible
    c. Complete
    d. Documented transfers
4. Comparison Samples
    a. Pyrolysis products
    b. Petroleum background
    c. Burned versus unburned samples
5. Sampling materials
    a. Recovering ignitable liquid residues from non-collectible, porous surfaces
    b. Non-clumping, non-scented kitty litter
    c. Other absorbent materials

4.3 CRITICAL TERMS

1. Absorbent
2. Chain of Custody
3. Comparison Sample
4. Control Sample
5. Microbial Degradation
6. Sample Matrix

4.4 READINGS AND REFERENCES

ASTM E 1492. **Standard Practice for Receiving, Documenting, Storing, and Retrieving Evidence in a Forensic Laboratory**, Current edition.

Belchior F, Andrews SP. **Evaluation of Cross-Contamination of Nylon Bags with Heavy-loaded Gasoline Fire Debris and with Automotive Paint Thinner.** J Forensic Sci. 2016; 61:1622-1631.

Bertsch W. **Volatiles from Carpet: A Source of Frequent Misinterpretation in Arson Analysis.** Journal of Chromatography. 1994; 674:329-333.

Borusiewicz R. **Comparison of new Ampac bags and FireDebrisPAK® bags as packaging for fire debris analysis.** J Forensic Sci. 2012; 57:1059-63.

Borusiewicz R., Kowalski R. **Volatile organic compounds in polyethylene bags – a forensic perspective.** Forensic Sci Int. 2016; 266:462-468.

Burda K, Black M, Djulamerovic S, Darwen K, Hollier K. **Field Test Kits for Collection of Ignitable Liquids and Ignitable Liquid Residues in Fire Debris**. Forensic Sci Int. 2016; 264:70-81.

DeHaan JD. **Pyrolysis Products of Structure Fires**. Journal of the Forensic Science Society. 1988; 28:299-309.

DeHaan JD, Skalsky FA. **Evaluation of Kapak Plastic Pouches.** Arson Analysis Newsletter. 1981; 5:6-11.

Dietz WP, Mann DC. **Evidence Contaminated by Polyester Bags**. Scientific Sleuthing Newsletter. 1998; 12 5-6.

Dietz WR. **Physical Evidence of Arson – Its Recognition, Collection and Packaging.** Fire & Arson Investigator. 1991; 33-39.

Demers-Kohls JF, Ouderkirk SL, Buckle JL, Norman EW, Cartwright NS, Dagenais C. **An Evaluation of Different Evidence Bags Used for Sampling and Storage of Fire Debris.** Canadian Society of Forensic Sciences Journal. 1994; 27:143-170.

Grutters MM, Dogger J, Hendrikse JN. **Performance testing of the new AMPAC fire debris bag against three other commerncal fire debris bags.** J Forensic Sci. 2012; 57:1290-8.

Henry CL. **Study of Nylon Bags for Packaging Fire Debris.** The CAC News. 2008; 4:30-32

Juhala J. **Contaminated Sample Containers?** Arson Analysis Newsletter. 1981; 5:57.

Kelly L. **Investigation Into the Validity of Using Nylon Bags for the Packaging of Exhibits Containing Fire Accelerants.** Home Office Forensic Science Laboratory, March to September, 1986; 21.

Kinard WD, Midkiff CM. **Arson Evidence Container Evaluation: II. "New Generation" KAPAK Bags.** J Forensic Sci. 1991; 36:1714-1721.

Kocisko MJ. **Absorption of Ignitable Liquids into Polyethylene/Polyvinylidine Dichloride Bags.** J Forensic Sci. 2001; 46:356-362.

Lang T. **A Study of Contamination in Fire Debris Containers.** Canadian Society of Forensic Sciences Journal. 1999; 75- 83.

Lentini J. **Control Samples, A Reply.** Fire & Arson Investigator. 1989; 39-40.

Mann DC, Putaansuu ND. **Alternative Sampling Methods to Collect Ignitable Liquid Residues from Non-porous Areas Such as Concrete.** Fire & Arson Investigator. 2006; 56:43-46.

Mann DC. **In Search of the Perfect Container for Fire Debris Evidence.** Fire & Arson Investigator. 2000; 30:21-25.

Newman R. **Forensic Fire Debris Analysis in Forensic Chemistry:Fundamentals and Applications**. John Wiley & Sons, Ltd. 2015.

NFPA 921, Guide for Fire and Explosion Investigations, National Fire Protection Association, Quincy, MA, (Chapter 9), Current Edition.

O'Donnell JF. **Reference Samples**. Fire & Arson Investigator. 1984; 40.

Position on Comparison Samples, International Association of Arson Investigators, Inc., Louisville, KY, Membership Committee, 1989-1990.

Rosenhan AK. **Let's Be Fair! The Case for Control Samples**. Fire & Arson Investigator. 1988; 31.

Sanderson JL, Baille CA, Baillet MA. **Sampling Techniques for Accelerant Residue Analysis.** Fire & Arson Investigator. 1990; 35-40.

Shiok WL. **Collecting Accelerants from Concrete**. Fire & Arson Investigator. 1985; 44, 46.

Stauffer E, Dolan J, Newman R. **Fire Debris Analysis**. Academic Press; 2008.

Tontarski RE**. Evaluation of Polyethylene Containers Used to Collect Evidence for Accelerant Detection.** J Forensic Sci. 1983; 28:440-445.

Tontarski RE. **Using Absorbents to Collect Hydrocarbon Accelerants from Concrete.** J Forensic Sci. 1985; 30:1230-1232.

Williams MR, Sigman M. **Performance testing of commercial containers for collection and storage of fire debris evidence**. J. Forensic Sci. 2007; 52:579-85.

4.5 STUDY QUESTIONS

1. Describe methods for storing and transporting fire debris including the pros and cons of each method.
2. What is the difference between a comparison and a control sample?
3. Why should comparison samples be collected?
4. What collection methods should be employed when it is not practical or possible to remove the sample matrix from the scene?
5. Where should samples be taken from if there is a pour pattern?
6. Is carpet or concrete a better sample? Why?
7. What is microbial degreadation as it relates to the analysis of ignitable liquids? How can proper storage minimize microbial degradation?

4.6 PRACTICAL EXERCISES

Goals of the exercise:

To collect ignitable liquid samples from non-removable, porous matrices utilizing numerous absorbent materials.

Procedure:

1. Obtain the following:
    a. Non-scented, non-clumping kitty litter
    b. Non-self rising flour
    c. Sand
    d. A variety of automotive oil absorbent products (i.e., granular, pads, etc.)
2. Prepare a set of control samples by placing each of the absorbent materials in appropriate evidence containers.
3. Prepare approximately 50 milliliters of standard accelerant mixture (SAM). SAM is a one to one (v/v) mixture of gasoline and diesel.
4. Place several milliliters of the test mixture in areas representing each of the absorbent materials on the following surfaces:
    a. Concrete
    b. Asphalt
    c. Tile
5. Cover each sample area with one of the absorbent materials for approximately one hour.
6. Prepare a set of comparison samples by placing each of the absorbent materials on each type of surface for approximately one hour.
7. Package each sample and comparison sample in an appropriate evidence container. Be sure to use clean tools to collect each sample.
8. Store the control, comparison and test mix items for analysis in a future practical exercise.

5 ANALYTICAL DATA GENERATION USING GC/MSD

5.1 OBJECTIVES

1. Describe selected ion monitoring and how extracted ions are selected.
2. Demonstrate how to properly interpret chromatographic and mass spectral data related to the analysis of ignitable liquids.
3. To develop an understanding of in-house methods of obtaining and cataloging ignitable liquid comparison samples.
4. To compile and classify a wide variety of commercially available ignitable liquid products.

5.2 TOPIC AREAS

a. Theoretical aspects
    i. History of chromatography
    ii. Introduction to the various chromatographic methods
    iii. Gas/liquid phase equilibrium
    iv. Van Deemter curves
    v. Cross contamination
    vi. Temperature vs. retention behavior

b. Chromatographic columns
    i. Liquid
    ii. Packed
    iii. Polar/non-polar
    iv. Column efficiency
    v. Resolution

c. Carrier Gas
    i. Gas selection
    ii. Flow rate
    iii. Troubleshooting

d. Detectors
    i. Thermal
    ii. Flame ionization
    iii. Photoionization
    iv. Mass Spectrometry
    v. Other

e. Quantitative evaluation
    i. Triangulation
    ii. Correlation of area and quantity
    iii. Peak characteristics

f. Qualitative evaluation

i. Peak pattern comparison (with standards)
ii. Instrument Coupling

g. Mass Spectrometer
    i. Comparison of GC detectors
        1. strengths and weaknesses
        2. sensitivity
        3. resolving power
    ii. Components
        1. vacuum systems
        2. GC/MS interfaces
        3. electron impact ionization
        4. chemical ionization
        5. mass separation methods
            a. quadrupole
            b. ion trap
            c. magnetic sector
            d. time of flight
            e. MS/MS
        6. detection/ion abundance determination
    iii. Operation and maintenance
        1. tuning and calibration
        2. routine maintenance

h. Basic Interpretation of Mass Spectral Data
    i. TIC
    ii. Molecular ions
    iii. Base peaks
    iv. Nitrogen rule
    v. Isotopic ratios
    vi. Fragmentation
    vii. Evaluation of the quality of mass spectral data
    viii. Libraries

i. Extracted Ion Chromatograms
    i. Chemical structure review
        1. alkanes
        2. alkenes
        3. aromatics
        4. naphthalenes

5. polynuclear aromatics
6. indanes and indenes
7. styrenes
8. terpenes

ii. Selected Ion Monitoring

1. selection of ions to monitor
2. use of ratios
3. pros/cons

iii. Comparison to standards and references

j. Sample Matrix Effects

i. "filtering" out interfering compounds
ii. microbial degradation in soil
iii. pyrolysis of polyethylene and other plastics
iv. wood thermal degradation

k. Internal standards

5.3 CRITICAL TERMS

There are no critical terms for this section.

5.4 READINGS AND REFERENCES

Ignitable Liquid Residue Analysis

Armstrong AT, Wittkower RS**, Identification of Accelerants in Fire Residues by Capillary Column Gas Chromatography**, J Forensic Sci. 1978; 23(4):662-671.

ASTM E 1618, **Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry**, Current edition.

Kelly R, Martz R., **Accelerant Identification in Fire Debris by Gas Chromatography/Mass Spectrometry Techniques**. J Forensic Sci.1984; 29(3):714-727.

Loscalzo PJ, DeForest PR, Chao JM. **A Study to Determine the Limit of Detectability of Gasoline Vapor from Simulated Arson Residues**. J Forensic Sci.1980; 25(1):162-167.

Manufacturer's equipment manuals

Newman R. **Forensic Fire Debris Analysis in Forensic Chemistry:Fundamentals and Applications.** John Wiley & Sons, Ltd. 2015.

Smith RM. **Mass Chromatograpic Analysis of Arson Accelerants.** J Forensic Sci. 1983; 28(2):318-329.

Smith RM. **Arson Analysis by Mass Chromatography**. Analytical Chemistry. 1982; 54(13):1399A-1409A.

Stauffer E, Dolan J, Newman R., **Fire Debris Analysis**. Academic Press. 2008.

Tontarski R, Strobe, R., **Automated Sampling and Computer Assisted Identification of Hydrocarbon Accelerants**. J Forensic Sci. 1982; 27(2):710-714.

Reference Ignitable Liquids

National Center for Forensic Science – **Ignitable Liquid Reference Collection** http://ilrc.ucf.edu/index.php

Newman R, Gilbert M, Lothridge K. **GC-MS Guide to Ignitable Liquids**. CRC Press. 1998.

Internal Standards

Locke, AK, Basara GJ, Sandercock PM. **Evaluation of internal standards for the analysis of ignitable liquid residues in fire debris**. J Forensic Sci. 2009; 54: 320-7.

5.5 STUDY QUESTIONS

1. What is the TIC?
2. What is ion profiling? Describe the difference between ion profiling and selected ion monitoring.
3. Describe how the macro sorts and presents data.
4. What compounds are most commonly used as internal standards in the analysis of fire debris? Describe different approaches to the use of internal standards in the analysis of fire debris.

5.6 PRACTICAL EXERCISES

Exercise 1: Effects of Temperature Program on Aliphatic and Aromatic Hydrocarbons

Goals of the exercise:

To determine how the temperature program affects aliphatic and aromatic hydrocarbons.

Procedure:

1. Prepare a dilute solution in carbon disulfide with internal standard of the following:
    a. ASTM E1618 test mix
    b. Standard Accelerant Mix (SAM)
2. Analyze the ASTM E1618 test mix and SAM using a standard fire debris method.
3. Analyze the ASTM E1618 test mix and SAM using an isothermal method.
4. Alter the method parameters of the standard fire debris method by either adjusting the flow or temperature ramp. Analyze the ASTM E1618 test mix and SAM using this experimental method.
    a. Be sure to save the experimental method as something other than the original method name.

Data Evaluation:

Using the data answer the following questions:

1. Describe the effects on aliphatic and aromatic hydrocarbons observed by using different GC methods.
2. What effects did your experimental method have on resolution? Was this consistent with lower and higher molecular weight compounds?

Exercise 2: Analysis of Ignitable Liquid Reference Materials

Goals of the exercise:

1. To become familiar with preparation of ignitable liquid references and analysis by GC/MS.
2. To become familar with the macro used for data analysis.

Procedure:

1. Obtain a reference sample for as many ignitiable liquid classes and sub-classes available in your laboratory.
2. Prepare a liquid dilution of each reference sample in carbon disulfide or other solvent appropriate for the reference sample. Use internal standard for each preparation.
3. Analyze each sample using the appropriate method by GC/MS. Methods may include a standard method, a solvent or low molecular weight method, and a high molecular weight method.
4. Print the data for each reference using the macro appropriate for the method.

6 IGNITABLE LIQUID RECOVERY METHODS & IGNITION TESTING

6.1 OBJECTIVES

1. To understand the advantages and disadvantages of the different methods for the recovery and separation of ignitable liquid residues in fire debris.
2. Perform analytical methods for recovery and classification of ignitable liquid residues.
3. To safely carry out ignition testing on suspected ignitable liquids.

6.2 TOPIC AREAS

a. Contamination Prevention
    i. Personal protective equipment
        1. Gloves
        2. Lab Coats
        3. Face Shields
        4. Fume Hoods
    ii. Ash or powdered material
        1. Disposable paper coverings

b. Preliminary Examinations
    i. Visual
        1. Evidence inventory
            a. Document
        2. Evaluate to determine which recovery procedure to use
        3. Check for the presence of incendiary devices or other evidence present
        4. May only be able to only do a cursory visual examination due to the risks of prolonged exposure to the air
    ii. Olfactory
        1. Always work in well ventilated area.
        2. Wafting the contents to evaluate the odor of ignitable liquids is not recommened due to the nature of potential chemicals in fire debris samples. However, strong ignitable liquid odors may be noted when the can has been opened without purposely smelling the sample.
        3. Odor of strong ignitable liquids may influence recovery method choice.
    iii. Procedure
        1. Note the condition of the container and whether or not it has been properly sealed. Note any damage which may have compromised the integrity of the container.
        2. Visually examine the item and note its contents (type of material or debris present) and condition (burned, partially burnt, burnt, etc.).
        3. If requested, examine for any evidence of incendiary materials or devices. If found, such materials may be subjected to additional examinations.

4. NOTE: Steps “2” and “3” may have to be postponed until after ignitable liquid recovery methods have been carried out if a significant amount of debris is present.
5. Record the results of these examinations in the laboratory notes.
6. Make sure the item is properly labeled with the laboratory case number and item designation.
7. If necessary, transfer the contents of the exhibit to a container suitable for the type of sampling method which will be used.

c. Headspace
    i. Room temperature and heated
    ii. Equipment needed
    iii. Advantages
    iv. Disadvantages
    v. Reference ASTM E1388

d. Passive Adsorption-Elution (PAE)
    i. Equipment needed
    ii. Adsorption considerations
        1. Amount of adsorbent needed
        2. Time and temperature of extraction procedure
        3. Displacement
        4. Carbon range limits
        5. Re-extraction of the sample vs. saving original adsorbent
    iii. Desorption considerations
        1. Safety of solvent
        2. Solvent choices
    iv. Advantages
    v. Disadvantages
    vi. Reference ASTM E1412

e. Solvent Extraction
    i. Equipment needed
    ii. Advantages
    iii. Disadvantages
    iv. Reference ASTM E1386

f. Solvent Wash
    i. Used with non-porous material
    ii. Best when visible liquid droplets can be seen
    iii. Same blanking procedure used in solvent extractions
    iv. Safety

v. Advantages

vi. Disadvantages

g. Solvent Dilution

i. Liquid samples are dissolved in an appropriate amount of solvent.

h. Ignition Testing

i. Equipment needed

ii. Good practice to determine if a liquid is ignitable

iii. Advantages

iv. Safety Considerations

1. Refer to ignition testing exercise

6.3 CRITICAL TERMS

1. Adsorption
2. Displacement
3. Dynamic Adsorption-Elution
4. Elution
5. Headspace Sampling
6. Ignition Testing
7. Passive Adsorption-Elution
8. Solid Phase Microextraction (SPME)
9. Solvent Extraction
10. Solvent Wash

6.4 READINGS AND REFERENCES

Andrasko J. **The Collection and Detection of Ignitable Liquid Vapors Using Porous Polymers and Curie Point Pyrolysis Wire Coated with Activated Charcoal**. J Forensic Sci. 1983; 28:330-334.

ASTM E1386, **Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Solvent Extraction**. Current edition.

ASTM E1388, **Standard Practice for Sampling of Headspace Vapors from Fire Debris Samples**, Current edition.

ASTM E1412, **Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration With Activated Charcoal**, Current edition.

ASTM E1413, **Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Dynamic Headspace Concentration**, Current edition.

ASTM E2154, **Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Solid Phase Microextraction (SPME),** Current edition.

Buckleton JS, Bettany BL, Walsh KAJ. **A Problem of Hydrocarbon Profile Modification by Charcoal**. J Forensic Sci. 1989; 34:449-453.

Caddy B, Smith CB, Macy J. **Methods of Fire Debris Preparation for Detection of Accelerants.** Forensic Science Review. 1991; 3:58-69.

Dietz WR. **Improved Charcoal Packaging for Ignitable Liquid Recovery by Passive Diffusion**. J Forensic Sci. 1991; 36:111-121.

Ettling CV. **Determination of Hydrocarbons in Fire Remains**. J Forensic Sci. 1963; 8 261-267.

Higgins, KM. **High Speed Extraction of Accelerants from Arson Debris**. J Forensic Sci. 1984; 29:874-880.

Juhala J. **A Method for Adsorption of Flammable Vapors by Direct Insertion of Activated Charcoal into the Debris Samples**. Arson Analysis Newsletter, 1982; 6:32-40.

Lentini JJ, Armstrong AT. **Comparison of the Eluting Efficiency of Carbon Disulfide with Diethyl Ether: The Case for Laboratory Safety.** J Forensic Sci. 1997; 42:307-311.

Newman R. **Forensic Fire Debris Analysis in Forensic Chemistry:Fundamentals and Applications.** John Wiley & Sons, Ltd. 2015.

Newman RT, Dietz WR, Lothridge MSM. **The Use of Activated Charcoal Strips for Fire Debris Extractions by Passive Diffusion. Part 1: The Effects of Time, Temperature, Strip Size, and Sample Concentration.** J Forensic Sci. 1996; 41:361-370.

Phelps JL, Chasteen CE, Render MM. **Extraction and Analysis of Low Molecular Weight Alcohols and Acetone from Fire Debris Using Passive Headspace Concentration.** J Forensic Sci.1994; 39:194-206.

Reeve V. **Developments in Arson Analysis: A Comparison of Charcoal Adsorption and Direct Headspace Injection Techniques Using Fused Silica Capillary Gas Chromatography**. J Forensic Sci. 1986; 31:479-488.

Rodgers CL, St. Pierre KA, Hall AB. **Recovery of Oxygenated Ignitable Liquids by Zeolites, Part II: Dual-mode Heated Passive Headspace Extraction.** Forensic Sci Int. 2014; 240:144-50.

St. Pierre KA, Desiderio VJ, Hall AB. **Recovery of Oxygenated Ignitable Liquids by Zeolites, Part I: Novel Extraction Methodology in Fire Debris Analysis.** Forensic Sci Int. 2014; 240:137-43.

Sandercock PML. **Comparison of Passive Charcoal Adsorption with a Dynamic Charcoal Adsorption Technique**. Canadian Society of Forensic Sciences Journal. 1994; 27:179-201.

Stauffer E, Dolan J, Newman R., **Fire Debris Analysis**. Academic Press. 2008.

Waters L, Palmer L. **Multiple Analysis of Fire Debris Samples Using Passive Headspace Concentration**. J Forensic Sci. 1993; 38:165-183.

Williams M R, Fernandes D, Bridge C, Dorrien D, Elliott S, Sigman M. **Adsorption Saturation and Chromatographic Distortion Effects on Passive Headspace Sampling with Activated Charcoal in Fire Debris Analysis**. J Forensic Sci. 2005; 50:316-325.

Yip IHL, Clair EG. **A Rapid Analysis of Ignitable Liquids in Fire Debris**. Canadian Society of Forensic Sciences Journal. 1976; 9:75-80.

6.5 STUDY QUESTIONS

1. Discuss the usage of charcoal adsorption-elution, headspace, solvent extraction, solid phase microextraction, and solvent wash. What type of samples work best with each of the extraction types? What are the advantages and disadvantages of each of the extraction types? Which techniques are used by our crime lab? Which techniques are not used by our lab and why?

2. How would heating temperature affect the chromatographic data in headspace and charcoal adsorption-elution techniques?
3. How does sample concentration affect the chromatographic data in headspace and charcoal adsorption-elution techniques?
4. What other adsorbents can be used to trap ignitable liquid residues in adsorption-elution techniques?
5. Is charcoal a good adsorbent for alcohol? For hydrocarbons?
6. What are the two basic types of desorption? Which is used for active charcoal and why?
7. What solvents can be used for ignitable liquid solvent extractions?
8. Discuss the factors that can lead to distorted recovery (discuss both skewing toward the light ends as well as toward the heavy ends) and how these factors can be minimized.
9. What additional steps must be added to the standard passive headspace concentration extraction for petroleum products if detection of alcohols and/or low molecular weight oxygenated solvents is desired?
10. Can kerosene and fuel oil #2/diesel fuel-type products be differentiated when passive headspace concentrations is the method of extraction? Explain.
11. Under what conditions is solvent extraction preferred over adsorption-elution extractions?
12. How can you determine if a liquid sample is aqueous or non-aqueous?
13. When and why would ignition testing be utilized?
14. A fire investigator suspects a sample of miscellaneous charred debris contains both an alcohol and a heavy product. How would you approach this analysis?

6.6 PRACTICAL EXERCISES

Exercise 1: Headspace (HS) versus Passive Adsorption-Elution (PAE)

Goals of the Exercise:

1. To become familiar with HS and PAE as techniques for extraction of fire debris samples.
2. To become familiar with challenges in the detection of ignitable liquids as the concentration and nature of the ignitable liquid changes using HS and PAE.

Procedure:

1. Prepare a triplicate set of lined quart cans for acetone, camping fuel, gasoline, charcoal starter (or paint thinner), and diesel fuel. One set should be labeled AHS (ambient headspace), one should be labeled HHS (heated headspace), and the final set labeled PAE at the following concentrations:
    a. 25 µL
    b. 50 µL
    c. 100 µL
    d. 250 µL
2. Place a Kim wipe or other absorbent toweling in each can. Pipette the appropriate IL at the designated concentration into each can. Secure a lid on each can as it is prepared to prevent cross-contamination.
3. PAE Samples

a. Using a clean scissors or a clean glass microscope slide split enough C-strips in half for each of the PAE samples.

b. Prepare a blank can to be used as a preparatory blank to demonstrate the can, strip, hook (or clip), solvents, and general process are free from interfering compounds.

c. Using the PAE set of cans and prep blank can, suspend one of the half charcoal strips on an hook or by alligator clip in each can. Be sure to change gloves and lab bench covering between each sample.

d. Heat the cans in a 60-80°C oven for a minimum of two hours.

e. While the cans are heating label autoliquid sampler vials (ALS) with sample information. Vials should either contain built in inserts or use ~400 µL inserts.

f. Remove the cans and allow them to cool to room temperature.

g. Remove the C-strips from each can and place in autoliquid sampler vial and elute with carbon disulfide containing internal standard. Prepare a corresponding blank for each sample. Be sure to change gloves and lab bench covering between each sample.

   i. Before placing the C-strips in the sample vial prepare the blanks. Rinse the sample vial with carbon disulfide and place this solvent into the blank vial.

   ii. C-strips may need to be folded or rolled to fit into the vial insert.

h. Analyze each blank and sample via GC/MS.

4. AHS Samples

   a. “Clean” the syringe by heating in a 60-90° oven for a few minutes. After heating allow the syringe to cool to room temperature. Pump the syringe several times with air.

   b. Withdraw 0.5 to 2.0 mL of air and inject into the GC for a blank. Analyze using a manual injection method.

   c. Create a hole in the can lid such that the syringe needle can be introduced. Seal the hole with tape.

   d. Puncture the syringe through the tape and withdraw 0.5 to 2.0 mL of headpace from the can.

   e. Immediately inject the headspace sample in the GC and analyze using a manual injection method.

   f. Reseal the hole in the can with tape to prevent volatile loss in case an additional sampling is required.

   g. While the sample is running on the GC, clean the syringe as described above in preparation for the next sample.

   h. Repeat until all AHS samples have been analyzed. Running a blank between each sample is not required but it is recommended that several blanks be run throughout this exercise to demonstrate whether or not the syringe cleaning procedure is effective.

5. HHS Samples

   a. Place the first HHS labeled can in a 60-90° oven for ~30 minutes.

b. "Clean" the syringe by heating in a 60-90° oven for a few minutes. After heating allow the syringe to cool to room temperature. Pump the syringe several times with air.

c. Withdraw 0.5 to 2.0 mL of air and inject into the GC for a blank. Analyze using a manual injection method.

d. Remove the sample can from the oven and do not wait for the can to cool. Create a hole in the can lid and cover with tape.

e. Puncture the syringe through the tape and withdraw 0.5 to 2.0 mL of headpace from the can.

f. Immediately inject the headspace sample in the GC and analyze using a manual injection method.

g. Reseal the hole in the can with tape to prevent volatile loss in case an additional sampling is required.

h. While the sample is running on the GC, clean the syringe as described above in preparation for the next sample.

i. Repeat until all HHS samples have been analyzed. Running a blank between each sample is not required but it is recommended that several blanks be run throughout this exercise to demonstrate whether or not the syringe cleaning procedure is effective.

Data Evaluation:

For each PAE, AHS, and HHS sample, evaluate the chromatrograms and mass spectral data produced by each general classof ignitable liquid and concentration level. Using the data answer the following questions:

1. As the concentration decreases, does one of the methods produce better results?
2. As the samples begin to contain larger molecules, does one of the methods produce better results?
3. What are the limitations of each method as samples contain larger molecules? Is there a practical limit to what can be "seen" in fire debris analysis?
4. Based on the data, which method would you choose to use and when? What are the advantages and disadvantages of each way of proceeding?

<u>Exercise 2: C-strip Size Evaluation for Passive Adsorption-Elution (PAE)</u>

Goals of the Exercise:

To determine if C-strip size affects the ability to effectively recover ignitable liquids using PAE.

Procedure:

1. Prepare a set of cans labeled ¼, ½, and 1.
2. Using a clean scissors or a clean glass microscope slide cut a C-strip to obtain a ¼ and ½ C-strip.
3. Place a Kim wipe or other absorbent toweling in each can. Pipette 50 µL of SAM into each can.
4. Prepare a blank can to be used as a preparatory blank to demonstrate the can, strip, hook (or clip), solvents, and general process are free from interfering compounds.
5. Suspend the C-strip in the appropriately labeled can with a hook or alligator clip. Secure the lid to each can.

6. Heat the cans in a 60-80°C oven for a minimum of two hours.
7. While the cans are heating label autoliquid sampler vials (ALS) with sample information. Vials should either contain built in inserts or use ~400 µL inserts.
8. Remove the cans and allow them to cool to room temperature.
9. Before placing the C-strips in the sample vial prepare the blanks. Rinse the sample vial with carbon disulfide and place this solvent into the blank vial.
10. Remove the C-strips from each can and place in autoliquid sampler vial and elute with carbon disulfide containing internal standard. C-strips may need to be folded or rolled to fit into the vial insert. Prepare a corresponding blank for each sample. Be sure to change gloves and lab bench covering between each sample.
11. Analyze each blank and sample via GC/MS.

Data Evaluation:

Evaluate the chromatogram and mass spectral data for each size of C-strip. Using the data answer the following questions:

1. How did the size of the C-strip affect recovery of the SAM?
2. Was recovery consistent across the range of lighter and heavier molecules for the different sized C-strips?

<u>Exercise 3: Effects of Heating Time on Sample Recovery for Passive Adsorption-Elution (PAE)</u>

Goals of the Exercise:

To evaluate the effects of heating time on sample recovery for PAE.

Procedure:

1. Prepare a set of cans labeled 30 minutes, 1 hour, 2 hours, 3 hours, 4 hours, 8 hours, 12 hours, 16 hours, 20 hours, 24 hours.
2. Place a Kim wipe or other absorbent toweling in each can. Pipette 50 µL of SAM into each can and suspend a whole C-strip into each can using a hook or an alligator clip.
3. Prepare a blank can to be used as a preparatory blank (PB) to demonstrate the can, strip, hook (or clip), solvents, and general process are free from interfering compounds.
4. Heat the cans in a 60-80°C oven for the prescribed amount of time.
5. While the cans are heating label autoliquid sampler vials (ALS) with sample information. Vials should either contain built in inserts or use ~400 µL inserts.
6. Remove the cans and allow them to cool to room temperature.
7. Before placing the C-strips in the sample vial prepare the blanks. Rinse the sample vial with carbon disulfide and place this solvent into the blank vial.
8. Remove the C-strips from each can and place in autoliquid sampler vial and elute with carbon disulfide containing internal standard. C-strips may need to be folded or rolled to fit into the vial insert. Prepare a corresponding blank for each sample. Be sure to change gloves and lab bench covering between each sample.
9. Analyze each blank and sample via GC/MS.

Data Evaluation:

Evaluate the chromatogram and mass spectral data for each sample. Using the data answer the following questions:

1. Describe the differences noted in the TIC for the range of heating times?
2. Which sample(s) appear to be most consistent with a neat/liquid reference of SAM?
3. What is your preferred heating time and why?

Exercise 4: Effects of Heating Temperature on Sample Recovery for Passive Adsorption-Elution (PAE)

Goals of the Exercise:

To evaluate the effects of heating temperature on sample recovery for PAE.

Procedure:

1. Prepare a set of cans labeled ambient, 35°, 50°, 60°, 70°, 80°, and 100°.
2. Place a Kim wipe or other absorbent toweling in each can. Pipette 50 µL of SAM into each can and suspend a whole C-strip into each can using a hook or an alligator clip.
3. Prepare a blank can to be used as a preparatory blank (PB) to demonstrate the can, strip, hook (or clip), solvents, and general process are free from interfering compounds.
4. Heat the cans at the prescribed temperature for two hours.
5. While the cans are heating label autoliquid sampler vials (ALS) with sample information. Vials should either contain built in inserts or use ~400 µL inserts.
6. Remove the cans and allow them to cool to room temperature.
7. Before placing the C-strips in the sample vial prepare the blanks. Rinse the sample vial with carbon disulfide and place this solvent into the blank vial.
8. Remove the C-strips from each can and place in autoliquid sampler vial and elute with carbon disulfide containing internal standard. C-strips may need to be folded or rolled to fit into the vial insert. Prepare a corresponding blank for each sample. Be sure to change gloves and lab bench covering between each sample.
9. Analyze each blank and sample via GC/MS.

Data Evaluation:

Evaluate the chromatogram and mass spectral data for each sample. Using the data answer the following questions:

1. Describe the differences noted in the TIC for the range of heating temperatures?
2. Consult with a DNA analyst and determine if the heating tempatures in this exercise could have a negative impact on evidence for DNA.
3. What is your preferred heating temperature and why?

Exercise 5: Solvent Extraction (SE) versus Passive Adsorption-Elution (PAE)

Goals of the Exercise:

1. To become familiar with solvent extractions as a technique for extraction of fire debris samples.
2. To compare the recovery of key compounds in ignitable liquids using SE and PAE.

Procedure:

1. Prepare a duplicate set of lined quart cans for acetone, camping fuel, gasoline, charcoal starter (or paint thinner), and diesel fuel. One set should be labeled SW and the other set labeled PAE.
2. Prepare one can as a preparatory blank for PAE and another can as a control for SW.
3. Place a like sized piece of wood in each can.
4. Apply 50 µL of each sample to the appropriately labeled sample cans.
5. PAE samples – analyze as described in previous exercises.
6. SW samples:
    a. Obtain a clean beaker sufficient to contain the sample.
    b. In a fume hood, thoroughly rinse the beaker with reagent grade pentane in a volume you estimate will be sufficient to cover the sample. Pour this sample onto a watch glass or evaporate in the beaker down to approximately 1 mL. Place this "blank" in labeled ALS vial.
        i. Note that while pentane is usually used, both carbon disulfide and methylene chloride have been used in this procedure. Carbon disulfide is avoided for considerations of health and environmental factors, and methylene chloride has not proved as successful for extraction.
    c. Place the sample in the rinsed beaker and add enough pentane to cover the sample. Allow the sample to soak in the pentane for a few minutes to extract ignitable liquid traces. Carefully pour off this solvent into a watch glass or another clean beaker. Evaporate the pentane down to about 1-2 mL and transfer to a labeled ALS vial.
        i. In actual casework, the appearance and viscosity of the extract may suggest halting evaporation at a larger volume. Filtration using glass wool in a clean disposable pipet may be necessary to remove particulate material from a concentrated extract.
    d. Analyze the blank and sample extracts using your standard GC/MS method.

Data Evaluation:

Using the data obtained, answer the following questions:

1. How well did the SE isolate the ignitable liquid residue?
2. How much were the SE results affected by background factors?
3. Is solvent extraction preferable to Passive Adsorption-Elution? When might you use SE?

<u>Exercise 6:Evaluating Absorbent Materials Used to Collect Ignitable Residues from Non-Removable Surfaces</u>

Goals of the Exercise:

To determine which absorbent material used to collect ignitable liquid residues is most effective.

Procedure:

1. Obtain the samples prepared in the Packaging and Preserving of Evidence, Comparison Samples, & Sampling Materials section of training.
2. Analyze the samples using PAE. Heat at 60-80°C for two hours.

Data Evaluation:

Using the data obtained, answer the following questions:

1. Which absorbent materials had the most background interference?
2. Which matrices had the most interference?
3. Which absorbent material recovered the gasoline-diesel mix most effectively?
4. Were gasoline and diesel equally recovered? Why or why not?

Exercise 7: Ignition Testing

Goals of the Exercise:

1. To safely carry out ignition testing on a variety of ignitable liquids.
2. To describe the flame color and smoke present during ignition of a variety of ignitable liquids.

Procedure:

This procedure must be carried out in a fume hood with no other flame sources. Minimal amounts of sample should be used.

1. Place two to three drops of an ignitable liquid sample on a watch glass or glass petri dish. Alternatively the ignitable liquid can be applied to glass wool placed on the watch glass or glass petri dish.
    a. If glass wool is used, dydinium glasses are useful for seeing the blue flames of oxygenated solvents.
    b. If a light oxygenated solvent is suspected, the glass wool can be omitted and the flame test done on a few drops of the liquid.
2. A lit match or other flame source is moved slowly toward the liquid until ignition occurs.
3. Note the color of the flame and the type of smoke generated, if they are visible.
4. After the liquid is consumed, note the type and color of any residue present.
5. If provided by your trainer, conduct ignition testing on unknown liquids.

Data Evaluation:

Using the data obtained, answer the following questions:

1. Can you associate flame color with a class or sub-class of ignitable liquid?
2. Can you associate the amount or color of smoke with the class or sub-class of ignitable liquid?
3. What was the relative carbon range of the ignitable liquids which were difficult to ignite?

7 DATA INTERPRETATION, INTERFERENCES, COMPARISON OF IGNITABLE LIQUIDS, DATA RECORDING

7.1 OBJECTIVES

1. To become familiar with the data generated by the recovery methods and the difficulties in interpreting the meaning of the data generated from complex fire environments.
2. Evaluate the effects of weathering on common ignitable liquids.
3. To become familiar with microbial degradation of common ignitable liquids.
4. Assess the applicability of determining common sources of two ignitable liquids.

7.2 TOPIC AREAS

1. Data Records/Notes
2. Data Analysis: GC/MS
    a. compound identification
    b. visual comparison (TIC)
    c. extracted ion chromatography (EIC)
    d. target compound chromatography (TCC)
3. Identification of Altered Ignitable Liquids
    a. evaporation
    b. microbial degradation
    c. vapor transfer
    d. sampling technique effects
4. Interference from Substrate Materials
    a. carpet and carpet padding
    b. wood and plant products
    c. paper products
    d. shoes and clothing
    e. polymers
    f. condensates
    g. vehicle fires
    h. others
5. Comparison of Ignitable Liquids
    a. gasoline
    b. aromatics in petroleum distillates
    c. oxygenated and miscellaneous products
    d. mixtures
6. Pyrolysis
    a. Mechanisms of degradation

i. Random scission
ii. Side group scission
iii. Depolymerization
iv. Other mechanisms and rearrangements

b. Commonly observed pyrolysis products

7.3 CRITICAL TERMS

1. Bi-modal Distribution
2. Microbial Degradation
3. Pyrolysis
4. Sample Matrix

7.4 READINGS AND REFERENCES

Almirall JR, Furton KG. **Characterization of Background and Pyrolysis Products that may Interfere with the Forensic Analysis of Fire Debris**. Journal of Analytical and Applied Pyrolysis. 2004; 71:51-67.

Armstrong A, Babrauskas V, Holmes MA, Martin C, Powell R, Riggs S, Young LD. **The Evaluation of the Extent of Transporting or "Tracking" an Identifiable Ignitable Liquid (Gasoline) Throughout Fire Scenes During the Investigative Process**. J Forensic Sci. 2004; 49:741-748.

ASTM E1618, **Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry**, current edition.

Baerncopf J, Hutches K. **A Review of Modern Challenges in Fire Debris Analysis**. Forensic Science Int. 2014: 244:e12-20. Doi 10.1016/j.forsciint.2014.02.017. Epub 2014 Apri1. PubMed PMID: 24780556.

Baerncopf JM, McGuffin VL, Smith RW. **Association of Ignitable Liquids Residues to Neat Ignitable Liquids in the Prescence of Matrix Interferences Using Chemometric Procedures**. J Forensic Sci. 2011; 56(1):70-81.

Barnes AT, Dolan JA, Kuk RJ, Siegel JA. **Comparison of Gasolines Using Gas Chromatography-Mass spectrometry and Target Ion Response**. J Forensic Sci. 2005; 49(5):1018-1023.

Bertsch W. **Volatiles from Carpet: A Source of Frequent Misinterpretation in Arson Analysis.** Journal of Chromatography. 1994:329-333.

Borusiewicz R, Kowalski R. **Volatile Organic Comounds in Polyethylene Bags – A Forensic Perspective.** Forensic Sci Int. 2016; 266:462-468.

Bruno TJ, Allen S. **Weathering Patterns of Ignitable Liquids with the Advanced Distillation Curve Method**. J Res Natl Inst Stand Technol. 2013; 118:29-51.

Cavanagh K, DuPasquier E, Lennard C. **Background Interference from Car Carpets-The Evidential Value of Petrol Residues in Cases of Suspected Vehicle Arson**. Forensic Sci Int. 2002;125:22-36.

Cavanagh-Steer K, DuPasquier E, Roux C, Lennard C. **The Transfer and Persistence of Petrol on Car Carpets.** Forensic Sci Int. 2005; 147:71-79.

Chalmers D. **Degradation of Gasoline, Barbecue Starter Fluid, and Diesel Fuel by Microbial Action in Soil**. Canadian Society of Forensic Sciences Journal. 2001; 34(2):49-62.

Clodfelter RW, Hueske EE. **A Comparison of Decomposition Products from Selected Burned Materials with Common Arson Accelerants**. J Forensic Sci. 1977; 22(1):116-118.

Contreras PA, Houck SS, Davis WM, Yu JCC. **Pyrolysis Products of Linear Alkylbenzenes – Implications in Fire Debris Analysis**. J Forensic Sci. 2013: 58(1):210-216.

Coulson SA, Morgan-Smith RK, Noble D. **The Effect of Compressed Air Foam on the Detection of Hydrocarbon Fuels in Fire Debris Samples**. Science and Justice. 2000; 4:257-260.

Daeid NN. **Fire Investigation**. CRC Press. 2004

DeHaan JD. **Pyrolysis Products of Structure Fires**. Journal of the Forensic Science Society. 1988: 28(5-6):299-309.

DeHaan JD, Campbell SJ, Nurbakhsh S. **Combustion of Animal Fat and Its Implications for the Consumption of Human Bodies in Fires**. Science and Justice. 1999; 39(1):27-38.

DeHaan JD, Taormina EI, Brien DJ. **Detection and Characterization of Volatile Organic Compounds from Burned Human and Animal Remains in Fire Debris**. Science and Justice. 2017; 57:118-127.

DeHaan JD, Large R. **Volatile Organic compounds from the Combustion of Human and Animal Tissue**. Science and Justice. 2004; 44(4):223-236.

Dolan JA, Stauffer E. **Aromatic Content in Medium Range Distillate Products – Part I: An examination of Various Liquids**. J Forensic Sci. 2004; 49(5):992-1004.

Ettling BV. **Analysis of Paraffin Wax in Fire Remains**. J Forensic Sci. 1975; 20:476-483.

Fire FL. **Plastics and Fire Investigations.** Fire Engineering. January 1985; 46-56.

Folkman TE, Kuehl AM, Groves RJ, Beveridge AD. **Evaporation Rate of Gasoline from Shoes, Clothing, Wood, and Carpet Materials and Kerosene from Shoes and Clothing**. Canadian Society of Forensic Sciences Journal. 1990; 23(2-3):49-59.

Guinther DA, Moss RD. **The Analysis and Identification of Weathered or Fire-aged Gasoline at Various Stages of Evaporation**. Arson Analysis Newsletter. 1983; 7(1):1-5.

Hetzel SS, Moss RD. **How Long After Waterproofing a Deck Can You Still Isolate an Ignitable Liquid?** J Forensic Sci. 2005: 50(2):369-376.

Holzer G, Bertsch W. **Recent Advances Toward the Detection of Accelerants in Arson Cases**. American Laboratory. 1988; 20(12):15-19.

Hirz R. **Gasoline Brand Identification and Individualization of Gasoline Lots**. Journal of the Forensic Science Society. 1989; 29(2):91-101.

Howard J, McKague AB. **A Fire Investigation Involving Combustion of Carpet Material**. J Forensic Sci. 1984; 29(3):919-922.

Hutches K**. Microbial Degradation of Ignitable Liquids on Building Materials**. Forensic Sci Int. 2013; 232:e38-e41.

Keto R. **GC/MS Data Interpretation for Petroleum Distillate Identification in Contaminated Arson Debris**. J Forensic Sci. 1995; 40:412-423.

Keto RO, Wineman PL. **Detection of Petroleum-Based Accelerants in Fire Debris by Target Compound Gas Chromatograph/Mass Spectroscopy**. Analytical Chemistry.1991; 63: 1964-1971.

Kirkbride KP. **Microbial Degradation of Petroleum Hydrocarbons: Implications for Arson Residue Analysis**. J Forensic Sci. 1992; 37(6):1585-1599.

Kuk RJ. **Analysis of Artificial Fireplace Logs by High Temperature Gas Chromatography**. J Forensic Sci. 2002; 47:1288-1293.

Lentini JJ. **Differentiation of Asphalt and Smoke Condensates from Liquid Petroleum Distillates Using GC/MS**. J Forensic Sci. 1998; 43(1):97-113.

Lentini JJ, Dolan JA, Cherry C. **The Petroleum-Laced Background**. J Forensic Sci. 2000; 45(5):968-989.

Mann DC. **Comparison of Automotive Gasolines using Capillary Gas Chromatography. I: Comparison Methodology**. J Forensic Sci. 1987; 32(2):348-357.

Mann DC. **Comparison of Automotive Gasolines Using Capillary Gas Chromatography. II: Limitations of Automotive Gasolines in Casework**. J Forensic Sci. 1987; 32(3):616-628.

Mann DC, Gresham WR. **Microbial Degradation of Gasoline in Soil**. J Forensic Sci. 1989; 35(4):913-923.

McGee E, Lang TL**. A Study of the Effects of a Micelle Encapsulator Fire Suppression Agent on Dynamic Headspace Analysis of Fire Debris Samples**. J Forensic Sci. 2002; 47(2):267-274.

Midkiff CR. **Is It a Petroleum Product? How Do You Know?** J Forensic Sci. 1986; 31(1):231-234.

Midkiff CR. **Brand Identification and Comparison of Petroleum Products – A Complex Problem**. Fire and Arson Investigator. 1975; 26 (2):18-21.

Newman R. **Forensic Fire Debris Analysis in Forensic Chemistry:Fundamentals and Applications**. John Wiley & Sons, Ltd. 2015.

O'Donnell JF. **Interferences from Backgrounds in Accelerant Residue Analysis**. Fire and Arson Investigator. 1989; 39(4):25-27.

Sandercock PML, Du Pasquier E. **Chemical Fingerprinting of Unevaporated Automotive Gasoline Samples.** Forensic Sci Int. 2003; 134:1-10.

Sandercock PML, Du Pasquier E. **Chemical Fingerprinting of Gasoline – 2.Comparison of Unevaporated and Evaporated Automotive Gasoline Samples.** Forensic Sci Int. 2003; 140:43-59.

Sandercock PML, Du Pasquier E. **Chemical Fingerprinting of Gasoline – 3.Comparison of Unevaporated Automotive Gasoline Samples from Australia and New Zealand**. Forensic Sci Int. 2003; 140:71-77.

Stauffer E, Dolan JA, Newman R. **Fire Debris Analysis**. Elsevier Inc. 2008

Stauffer E. **Concept of Pyrolysis for Fire Debris Analysts**. Science and Justice. 2003; 43(4):1-12.

Stone IC, Lomonte MS. **False Positives in Analysis of Fire Debris**. Fire and Arson Investigator.1984; 34(3):36-40.

Trimpe MA. **Turpentine in Arson Analysis**. J Forensic Sci. 1991; 36(4):1059-1073.

Turner DA, Goodpaster JV. **Comparing the Effects of Weathering and Microbrial Degradation on Gasoliune Using Principal Components Analysis**. J Forensic Sci. 2012; 57(1):64-69.

Turner DA, Goodpaster JV. **The Effects of Season and Soil Type on Microbial Degradation of Gasoline Residues from Incendiary Devices**. Anal Bioanal Chem. 2013; 405:1593-1599.

Turner DA, Goodpaster JV. **The Effects of Microbial Degradation on Ignitable Liquids**. Anal Bioanal Chem. 2009; 394:363-371.

Turner DA, Williams M, Sigman MA, Goodpaster JV. **A Comprehensive Study of the Alteration of Ignitable Liquids by Weathering and Microbial Degradation**. J. Forensic Sci. 2018; 63(1). doi: 10.1111/1556-4029.13527

Wallace JR. **GC/MS Data from Fire Debris Samples: Interpretation and Applications.** J Forensic Sci. 1999; 44(5):996-1012.

Wells SB. **The Identification of Isopar H in Vinyl Flooring**. J Forensic Sci. 2005; 50(4):865-872.

Wineman PL, Keto RO. **Target Compound Method for the Analysis of Accelerant Residues in Fire Debris**. Analytica Chimica Acta. 1994; 288(1-2):97-110.

Winters K, Evans M. **Effects of Burning and Mold Growth on the Chemical Composition of Firelog Fuels**. J Forensic Sci. 2016; 61(4):1085-92.

7.5 STUDY QUESTIONS

1. What are the effects that evaporation/weathering will have on the appearance of ignitable liquid data?
2. Describe microbial degadation as it relates to ignitable liquids. Which microbes are involved in the process? Which compounds are more likely to be impacted by microbial degradation? How can microbial degradation be minimized in evidence samples?
3. How might different sampling methods affect the appearance of ignitable liquid data?
4. What impact might different substrates have on the appearance of fire debris data?
5. When are comparisons of ignitable liquids possible? What are the strengths and limitations of those comparisons?
6. Describe three mechanisms associated with pyrolysis. What compounds or patterns of compounds would you expect to see with each mechanism?
7. Research methods of fire suppression. How might products used in fire suppression interfere with the interpretation of ignitable liquid residues?

7.6 PRACTICAL EXERCISES

Exercise 1: Burned Matrix Study

Goals of the exercise:

To process, extract, analyze and evaluate the data from a series of common “background” items.

Procedure:

1. Collect a variety of materials to be analyzed. Material selection should include a variety of building materials, clothing/fabric items, household/office products. The following is a minimum list of materials which should be collected:
    a. Newspaper
    b. Soda or cereal boxes
    c. Cardboard boxes
    d. Magazines pages
    e. Resealable plastic bags
    f. Polyethylene sheet plastic wrap
    g. Plastic food containers
    h. “Egg crate” foam padding

i. Styrofoam
j. Carpet padding
k. Carpet samples (nylong, polypropylene, blended materials)
l. Roof shingles
m. Linoleum flooring
n. Vinyl flooring
o. Hardwood flooring
p. PEX pipe
q. Foam mattresses or cushions
r. Old leather shoes
s. Athletic shoes
t. Pine wood, pinecones, and/or pineneedles
u. Hardwood
v. Laminated wood
w. Worn clothing

2. Prepare two sets of new paint cans for each type of material to be analyzed. The paint cans should be appropriately sized for the sample. Samples may need to be cut to fit in the cans. One set will be "as is" samples. The other will be "pyrolyzed" samples.
3. For each of the "pyrolyzed" samples, in a fume hood or in a safe outdoor area carefully ignite the sample with a propane torch. Allow the sample to burn for several minutes before extinguishing the sample. Samples can be extinguished by lightly placing the lid on the paint can.
4. Suspend a C-strip in each can and proceed with the normal PAE procedure. Be sure to allow the pyrolyzed cans to cool before preparing them for PAE.
5. Extract the C-strips and analyze by GC/MS.

Data Evaluation:

Using the data answer the following questions.

1. Compare the data from the "as is" and "pyrolyzed" samples. What are the similiarities and differences observed?
2. Determine what types of compounds may be contributed by the background materials. References such as "The Petroleum Laced Background", "Volatiles from Carpet: A Source of Frequent Misinterpretation in Arson Analysis", "Pyrolysis Products of Structure Fires", and "Concept of Pyrolysis for Fire Debris Analysts" will be helpful.
3. What information would you like to have about case samples before forming a conclusion?

<u>Exercise 2: Weathering of Common Ignitable Liquids</u>

Goals of the exercise:

To determine how weathering will change the composition of ignitable liquids.

Procedure:

At a minimum gasoline and a petroleum distillate will be used for this exercise. If time does not allow for the weathering portion of this exercise, weathered kerosene and gasoline kits may be available from vendors such as Restek.

1. Collect an unweathered sample of the ignitable liquid and place in a labeled storage vial.
2. Working in a fume hood measure 1 L of ignitable liquid in a graduated cylinder. This can be done on a smaller scale but will result in less sample for the future use or for the reference collection.
3. Allow the ignitable liquid to evaporate and collect approximately 1 mL amounts at the designated levels of evaporation. This process will take time and toward the end may require the addition of some heat to facilitate evaporation. A watch glass can be placed over the top of the cylinder to slow evaporation overnight or on the weekend.
    a. 25% weathered
    b. 50% weathered
    c. 75% weathered
    d. 90% weathered
    e. 99% weathered
4. Analyze each of the samples by GC/MS.
5. The created samples may be added to the reference collection for future use.

Data Evaluation:

Using the data answer the following questions.

1. At what level did the pattern of the ignitable liquid change significantly as compared to the unweathered sample?
2. Can you still determine the ignitable liquid at 90% or 99% weathered based on the TIC? on the EIC?
3. Why is it a good idea to include weathered samples in your reference collection?

<u>Exercise 3: Microbial Degredation on Ignitable Liquids</u>

Goals of the exercise:

1. To determine how gasoline and hydrocarbon mixtures degrade over time when exposed to common soil bacteria.
2. To evaluate storage conditions on microbial action.

Procedure:

1. Obtain healthy top soil. Bags of potting soil may be used but they may be less effective than healthy soil from a garden or planting bed.
2. Label twenty-seven quart cans as follows:

	Ambient	Fridge	Freezer
Blank	Day 0		
Gasoline	Day 0		
	Day 2	Day 2	Day 2
	Day 4	Day 4	Day 4

	Day 7	Day 7	Day 7
	Day 14	Day 14	Day 14
MPD	Day 0		
	Day 2	Day 2	Day 2
	Day 4	Day 4	Day 4
	Day 7	Day 7	Day 7
	Day 14	Day 14	Day 14

3. Add 250 grams of soil to each can.
4. Pipete approximately 200 microliters of ignitable liquid to each can as appropriate.
5. Extract the blank and Day 0 cans by PAE immediately. Remove the C-strips and store in labeled vials until all the samples in this exercise are ready to be analyzed by GC/MS.
6. Store the other cans as labeled.
7. Extract by PAE on the appropriate days. Remove the C-strips and store in labeled vials until all the samples in this exercise are ready to be analyzed by GC/MS.
8. Analyze all strips by GC/MS.

Data Evaluation:

Using the data answer the following questions.

1. Were any ignitable liquids detected in the “blank” soil sample?
2. What changes have occurred over time?
3. How did storing under refrigeration versus freezing alter microbial activity?
4. If other trainees are completing this exercise compare the results. Were the results consistent? Be aware that different species of bacteria will consume components selectively and that results may not be reproducible from one soil set to another.

8 INCENDIARY DEVICES, UNUSUAL EVIDENCE, AND SPECIAL SITUATIONS

8.1 OBJECTIVES

1. To analyze a variety of biofuels and become familiar with extraction techniques for this type of evidence.
2. To familiarize the trainee with commonly-seen incendiary devices, such as Molotov cocktails and issues related to their analysis.
3. To become familiar with incendiary mixtures that do not involve ignitable liquids and issues related to the preservation of their residues and their analysis.
4. To create awareness of situations in which other types of forensic analysis may be required in addition to ignitable liquid analysis and how to work with other scientists to prioritize analyses and best preserve the evidentiary value of submitted exhibits.

8.2 TOPIC AREAS

1. Incendiary Devices
    a. Types of Incendiary Devices
    b. Components of Incendiary Devices
        i. Container
            1. Wick
            2. Sealant
            3. Fuel
            4. Timer (if any)
            5. Igniter
    c. Common Incendiary Mixtures
        i. Thermite
        ii. Pool chlorine and brake fluid
        iii. Napalm
        iv. Safety flares (fusees)
        v. Gelled fuels
        vi. Others
2. Unusual Evidence
    a. Inhalants
    b. Sprays
    c. Ignitable liquids in non-fire cases
        i. Unknown materials
        ii. Product tampering
    d. Others
3. Vegetable Oils and Fats
        i. Comprised primarily of trigylcerides and some free fatty acids

ii. These compounds are not easily analyzed by traditional ignitable liquid extraction techniques

iii. Generally require extraction and derivatization to fatty acid methyl esters (FAME) in order to identify by GCMS.

iv. Identification of specific types of oils (olive, corn, linseed, etc.) requires quantitative analysis of the fatty acid esters and this type of testing will not be conducted.

v. ASTM E2881 details extraction and derivatization for identification of vegetable oils and fats. This is a destructive method and should only be used following traditional ignitable liquid extraction techniques.

4. Other types of analysis on fire debris evidence
    a. Explosives
    b. Other chemical analyses
        i. pepper spray et al.
        ii. strong acids
        iii. general chemical analysis
    c. Latent prints
    d. DNA
    e. Trace
        i. shoewear impressions
        ii. physical matches
        iii. trace evidence
    f. Documents
    g. Firearms
    h. Computers
5. Planning the Analytical Sequence
    a. Evaluation and Consultation
    b. Prioritization
    c. Packaging
6. Special Situations

8.3 CRITICAL TERMS

1. Incendiary device
2. Molotov cocktail
3. Incendiary mixture
4. Thermite
5. Pyrophoric
6. Gelled fuel

8.4 READING AND REFERENCES

ASTM E2881, **Standard Test Method for Extraction and Derivatization of Vegetable Oils and Fats from Fire Debris and Liquid Samples with Analysis by Gas Chromatography-Mass Spectrometry**, current edition.

ASTM E2997. **Standard Test Method for Analysis of Biodiesel Products by Gas Chromatography-Mass Spectrometry**, current edition.

Bertsch W, Holtzer G, Sellers C. **Chemical Analysis for the Arson Investigator and Attorney**. Heidelberg; Hüthig Verlag GmbH; 1993.

Coulson SA, Morgan-Smith RK. **The Transfer of Petrol on to Clothing and Shoes While Pouring Petrol Around a Room**. Forensic Sci Int. 2000;112:35-141.

Dean WL. **Examination of Fire Debris for Flare (Fusee) Residues by Energy Dispersive X-Ray Spectrometry**. Arson Analysis Newsletter. 1984; 8:23-46.

DeHaan J. **Kirk's Fire Investigation**. Upper Saddle River, New Jersey: Prentice Hall; current edition.

Earth Liberation Front. **Setting Fires With Electrical Timers: An Earth Liberation Front Guide**. Fireant Collective. 2001.

Fusees get extremely hot, leave telltale signs of their presence. Fire Findings. 1995; 3(2):5.

Gambrel AK, Reardon MR. **Extraction, Derivatization, and Analysis of Vegetable Oils from Fire Debris**. 2008; 53(5):1372-80.

Goodman MR, Kaley EA, Finney, EE. **Forensic Analysis of Biodiesel**. Forensic Sci. Int. 2016; 263:10-26.

Hutches K, Lord J. **A New Kind of Molotov? Gasoline-Pool Chlorinator Mixtures**. J Forensic Sci. 2012; 57(4):1064-1069.

Kuk RJ, Spagnola MV. **Extraction of Alternative Fuels from Fire Debris Samples**. J Forensic Sci. 2008; 53(5):1123-9.

Midkiff CR. **Arson and explosive investigation**. in: Saferstein, R, ed. Forensic Science Handbook, Vol. I. Upper Saddle River, New Jersey: Prentice-Hall; current edition.

National Fire Protection Association. **NFPA 921: Guide for Fire and Explosion Investigations**. Quincy, Massachusetts: NFPA; current edition.

Powell W. **The Anarchist Cookbook**. Any edition.

Saxon K. **The Poor Man's James Bond**. Desert Publications, any edition.

Schmidt M. **Thermite: The Smoking Gun**. Republic Magazine. 2010; 16:30-31.

Schwenk LM, Reardon MR. **Practical Aspects of Analyzing Vegetable Oil in Fire Debris**. J Forensic Sci. 2009; 54(4):874-880.

Shelef R, et al. **Development of Latent Fingerprints from Incendiary Bottles**. J Forensic Identification. 1996; 46(5):556-69.

Stauffer E. **A Review of the Analysis of Vegetable Oil Residues from Fire Debris Samples: Analytical Scheme, Interpretation of the Results, and Future Needs.** J Forensic Sci. 2006; 51(5):1016-1032.

Stauffer E, Byron D. **Alternative Fuels in Fire Debris Analysis: Biodiesel Basics**. J Forensic Sci. 2007; 52(2):371-379.

WSP Crime Laboratory Trace Evidence Technical Procedures and Training Manual

Wells C, Lee JR, Hooban C, Vo W**. Identification and Development of a Gelled Fuel Through the Use of Liquid Gelling Agents.** Naval Surface Warfare Center. 2008.

8.5 STUDY QUESTIONS

1. What are fatty acid methyl esters?
2. How would you perform an acid-catalyzed derivatization of triglycerides? A base-catalyzed derivatization of triglycerides?
3. What does PUFA stand for? Give examples of PUFAs. What types of oils would be considered self-heating oils?
4. What are the concerns with the analysis of a Molotov cocktail? What other types of analysis might be needed and how can they be accommodated?
5. What are the concerns with the analysis of incendiary devices in general? What other types of analysis might be needed? What are the needs and concerns of those types of analyses?
6. Research two different ways to make gelled fuels that would be available to the average person.
7. What kind of physical evidence might a fire investigator encounter in a fire caused by a hypergolic mixture? How should this evidence be collected and packaged? How might this evidence be analyzed in the lab?
8. How might ignitable liquid analysis compromise certain types of evidence? How might it affect other forensic analyses?
9. How might analysis by other forensic disciplines compromise evidence for ignitable liquid analysis?
10. How will the way an item is packaged and stored affect the analysis by various forensic disciplines?

8.6 PRACTICAL EXERCISES

Exercise 1: Analysis of Vegetable Oils and Fats

Goals of the exercise:

1. To become familiar with the extraction and derivatization of vegetable oils and fats from fire debris and liquid samples as described in ASTM E2881.
2. Analyze biodiesel products as described in ASTM E2997.

Procedure:

1. Obtain several different types of vegetable oils and fats, FAME reference materials, and the chemicals needed for acid and base catalyzed derivatization using ASTM E2881.
2. Perform both acid and base catalyzed derivatizations on the samples using ASTM E2881. You may need to alter a GC/MS method to perform this analysis.

Data Evaluation:

Using the data answer the following questions:

1. What compounds were detected in the analyzed samples?
2. Which derivatization technique was more effective?
3. How would you document your conclusions for these samples in a report?

Practical Exercise 2: Gelled Fuels

Goals of the exercise:

To prepare a gelled fuel and analyze the product.

Procedure:

1. Prepare a gelled fuel using one of the methods researched in the study questions.
2. Analyze the gelled fuel using an appropriate extraction technique and GC/MS.

Data Evaluation:

Using the data answer the following questions:

1. What were the challenges in extracting the gelled fuel?
2. Did you detect the ignitable liquid?
3. Could you detect by GC/MS the other compounds used to prepare the gelled fuel? If not, which analytical techniques would be useful in identifying the other compounds used to prepare the gelled fuel

Practical Exercise 3: Mock Consultations

Goals of the exercise:

1. To evaluate several types of potential fire debris evidence to determine what types of additional analyses could be potentially require.
2. To consult with scientists in other functional areas and develop one or more strategies to accommodate as many analytical needs as possible based on the case scenario and needs of the submitting agency.

Procedure:

Consider the following examples of evidence. For each example, try to think of what other types of analysis might be needed by the investigator. Try to think of the order of priority these analyses might have. Consult with scientists in the appropriate functional areas to determine their needs and concerns with analysis of the item. Develop one or more schemes of analysis for each item, depending on the possible needs of the investigator.

a. Suspect athletic shoes with bloodstains.
b. Molotov cocktail remains – bottle neck with a twisted piece of t-shirt in it.
c. Gasoline can fragments with a disrupted pipe bomb taped to it.

Practical Exercise 4: Case Studies

Goals of the exercise:

1. To evaluate several types of potential fire debris evidence and determine what types of additional analyses could potentially be required.
2. To consult with scientists in other functional areas and develop one or more strategies to accommodate as many analytical needs as possible based on the case scenario and needs of the submitting agency.

Procedure:

Ask two or three fire debris analysts other than the trainer to discuss a few of their more unusual cases. Find out how the scientist handled the analysis and if other functional areas were involved.

9 QUALITY ASSURANCE, SAMPLE PRESERVATION, REPORT WRITING, AND CASE DOCUMENTATION

9.1 OBJECTIVES

1. To become familiar with the quality assurance elements associated with ignitable liquid analysis.
2. Determine how ignitable liquid samples should be preserved for long term storage.
3. To demonstrate a basic understanding of report writing.
4. To become familiar with the variety of documentation required to be included in an ignitable liquid residue case.

9.2 TOPIC AREAS

1. Quality Assurance
    a. Equipment
        i. Thermometers and/or ovens
        ii. GC/MSDs
        iii. Pipettes
    b. Solvents
    c. C-strips
    d. Reference material
2. Sample Preservation
    a. Extraction type
        i. PAE
            1. Single-strip adsorption
                a. Whole strip
                b. Split strip
            2. Two-strip adsorption
        ii. Solvent Extraction
        iii. Headspace
    b. Packaging of samples
    c. LIMS requirements
3. Report Writing
    a. Report format
    b. Conclusions
        i. Consistent with ASTM E1618 and E2881.
        ii. Give an opinion whether an ignitable liquid was present or not.
        iii. Disclaimers for positive and negative cases
        iv. Examples of possible sources for positive cases
        v. Comparison samples

c. Evidence
    i. Description of the evidence
    ii. Packaging issues
d. Methods
    i. Extractions
    ii. Instrumental analysis
    iii. Ignition testing
    iv. Other chemical testing
e. Statement regarding sample preservation

4. Case documentation
    a. RFLE
        i. Adding new items
    b. Notes
    c. Instrumental data
    d. Reference materials
    e. Data disc

9.3 CRITICAL TERMS

There are no critical terms for this section.

9.4 READING AND REFERENCES

ASTM E1618, **Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry**, current edition.

ASTM E2451, **Standard Practive for Preserving Ignitable Liquids and Ignitable Liquid Residue Extracts from Fire Debris Samples**, current edition.

WSP CLD LIMS Operations Manual

WSP CLD Materials Analysis Technical Procedures

WSP CLD Quality/Operations Manual

9.5 STUDY QUESTIONS

1. You have run out of the carbon disulfide you use for PAE. Describe how you would test and prepare a new bottle of carbon disulfide which will include an internal standard.
2. How will you verify the thermometer that is either built into to your oven or used in the oven is working properly?
3. Describe how you would preserve the following types of extracts for long term storage:
    a. A single C-strip which was analyzed whole
    b. A single C-strip which was split for analysis
    c. Pentane in a vial insert from a solvent extraction
4. What must be done in LIMS and on the RFLE to document the creation of samples for long term storage?
5. How would you word the conclusion in a report for the following situations:

a. Charred fabric found to contain terpenes
b. Terpenes in charred soil and vegetative material consistent with pine needles
c. Toluene on shoes
d. Gasoline in a soil sample which had undergone microbial degradation
e. Weak medium petroleum distillate in an exhibit in which the lid was not properly seated on the can
f. Paraffin wax
g. A mixture of a light aromatic and a heavy petroleum distillate

6. Is there a difference between 'no ignitable liquids detected' and 'no ignitable liquids identified'? Give examples of when you may use one or both of these phrases?

9.6 PRACTICAL EXERCISES

Exercise 1: Case Review

Goals of the exercise
To review a variety of completed ignitable liquid cases to become familiar with how the report is written, what supporting documentation is included, and how the complete file is put together.

Procedure:

1. Review five to ten complete ignitable liquid casefiles from a variety of analysts to determine how each puts their case file together.
2. Document the cases which were reviewed and your general observations about the case files.

Exercise 2: Unknowns- Putting it All Together

Goals of the exercise:

1. To demonstrate appropriate method selection, extraction, analysis and interpretation of data.
2. To practice report writing and compiling technical data.

Procedure:

1. Your trainer will provide you with a series of samples and a mock RFLE.
2. Evaluate the samples and analyze as appropriate.
3. Prepare your casefile and write a report.

FIRE DEBRIS TRAINING CHECKLIST - PAGE 1

Trainee:		Trainer:		
		Trainee Initials/Date	Trainer Initials/Date	Time for Completion
Overview of Fire				
	Reading			
	Critical Terms			
	Study Questions			
Sources and Classifications of Ignitable Liquids				
	Reading			
	Critical Terms			
	Study Questions			
	Practical Exercises			
Packaging and Preserving Evidence, Comparison Samples & Sampling Materials				
	Reading			
	Critical Terms			
	Demonstration/Observation			
	Study Questions			
	Practical Exercises			
Analytical Data Generation Using GC/MSD				
	Reading			
	Demonstration/Observation			
	Study Questions			
	Practical Exercises			
Ignitable Liquid Recovery Methods & Ignition Testing				
	Reading			
	Critical Terms			
	Demonstration/Observation			
	Study Questions			
	Practical Exercises			

FIRE DEBRIS TRAINING CHECKLIST - PAGE 2

Trainee:		Trainer:		
		Trainee Initials/Date	Trainer Initials/Date	Time for Completion
Data Interpretation, Interferences, Comparison of Ignitable Liquids & Data Recording				
	Reading			
	Critical Terms			
	Demonstration/Observation			
	Study Questions			
	Practical Exercises			
Incendiary Devices, Unusual Evidence and Special Situations				
	Reading			
	Critical Terms			
	Demonstration/Observation			
	Study Questions			
	Practical Exercises			
Quality Assurance, Sample Preservation, Report Writing, and Case Documentation				
	Reading			
	Study Questions			
	Practical Exercises			
Written Examination				
Competency Testing				
Mock Trial				