Fire Debris Analysis

1. Scope

This method is used for the analysis, classification, and comparison of ignitable liquids and residues from fire related evidence.

2. Terms and definitions

Adsorption- trapping of gaseous materials on the surface of a solid substrate.

ASTM International- formerly known as the American Society for Testing and Materials (ASTM) is a globally recognized leader in the development and delivery of international voluntary consensus standards.

ASTM 1618 Column Resolution Test Mixture- a thirteen component mixture (including C6 thru C20) used to performance check the gas chromatograph-mass spectrometer.

Blank - An analytical control consisting of the solvent carbon disulfide. It is used to ensure that there is no carryover on the GC/MS and that no components are present that will interfere with analysis. It is run prior to the start of a sequence and between samples.

3. References

ASTM E 1618, Standard Guide for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography – Mass Spectrometry

ASTM E 1412, Practice for Separation and Concentration of Flammable and Combustible Liquid Residues from Fire Debris Samples by Passive Headspace Concentration

ASTM E 1386, Practice for Separation and Concentration of Flammable or Combustible Liquid Residues from Fire Debris by Solvent Extraction

ASTM E 1388, Practice for Sampling of Headspace Vapors from Fire Debris Samples

4. Examination Procedures

4.1. Evidence Types

Any debris or evidence from a fire scene, subject and victim clothing, and items removed from a subject with possible connections to a fire scene such as gas cans and automobile floor mats. In addition, other evidence may be submitted, not associated with a possible arson, requesting the analysis for ignitable liquids.

4.2. Instruments and Equipment

Gas Chromatograph/Mass Spectrometer, capable of scanning at least 40-400 m/z, equipped with methylsilicone or phenylmethylsilicone columns. The GC/MS system must be able to retrieve a specified mass spectral scan for a data file and compare it against a library of mass spectra available to the data system.
Temperature controlled Oven(s) with a National Institute of Standards and Technology (NIST) traceable thermometer
Cotton String
Paper Clips
Tweezers
Razor Blades or Scalpel Blades
Clean Paint Cans with Lids
Disposable Pipettes
Autosampler Vials and caps
Liquid and Gas Syringes
Hammer or mallet
Large Pans and Beakers
Tape
Photographic equipment with accessories

4.3. Reagents and Chemicals

Carbon Disulfide (CS_2)
C_{22} (N-Docosane)/Carbon Disulfide (CS_2) Solution
ASTM 1618 Column Resolution Test Mixture
Charcoal Strips or ACS (Albrayco Laboratories)
Commercially Available Reference Library of Ignitable Materials

All chemicals and reagents are ACS reagent grade or better unless otherwise specified.

4.4. Reagent Preparation

C_{22} (N-Docosane)/Carbon Disulfide Solution (CS_2) – Mix 500 mg of C_{22} in 50 ml of Carbon Disulfide (CS_2).

ASTM 1618 Column Resolution Test Mixture – Add 1 vial of the ASTM 1618 Column Resolution Test Mixture to a 10 mL volumetric flask and bring up to volume with Carbon Disulfide.

4.5. Quality Control/Quality Assurance

Each lot of carbon disulfide must be checked for purity by evaporating a sample of the solvent to one half the original volume and analyzing the evaporated solvent in the same manner as submitted cases. This chromatogram will be maintained in the Reagent Verification Book. If the carbon disulfide is contaminated, consult with Unit Supervisor for next steps.

Each lot of carbon strips shall be contamination checked by placing a portion of a new strip in an autosampler vial and eluting with carbon disulfide. Analyze the eluent the same as casework. Each lot of carbon strips shall also be adsorption checked by placing approximately 5 µL of a known ignitable liquid on a clean Kimwipe or cotton ball in a clean quart metal can. The can will be analyzed the same as casework. The chromatograms will be maintained in the Microanalysis Unit of the laboratory. If the carbon strips are contaminated or faulty, these strips will not be used. Consult with Unit Supervisor for next steps.

Analyze the newly prepared reagents on the Gas Chromatograph/Mass Spectrometer (GC/MS). Maintain the chromatograms in the Reagent Verification Book. If the C_{22} is not present in the chromatogram, remake with the original chemicals and retest. If the any of the components in the test mixture are not present in the chromatogram, remake with a new vial of solution and retest. Consult with the Unit Supervisor should the reagent fail again.

Reference Ignitable Liquids must be analyzed in the same manner as submitted cases

Evidence identified as negative control samples that are received into the laboratory from an officer will be treated the same as all other fire debris evidence and reported as such. Sometimes, an officer will submit an empty container to be analyzed to verify the cleanliness of a batch of containers. The results of this analysis will be reported directly to the officer and not included in an Official Report.

An autotune will be run on the GC/MS each day the instrument is used.

All sample and control vials generated from casework will be maintained in a designated area that is secure and has limited access. These vials will be stored properly sealed in boxes, uniquely identified with barcodes attached, and electronically transferred to Microanalysis Long Term Storage where they will be retained indefinitely.

4.6. Procedural and Chemical Precautions

Refer to the TBI Safety Manual for general safety requirements and hazard information regarding the use of reagents and solvents, and overall safety guidelines.

Protective attire, including laboratory coat, mask, gloves and eye protection should be used when working with clothing and/or bloodstained items.

Decontamination of a scientist's work area should be performed after each use, but shall be done after analyzing bloodstained items.

Hazardous chemicals shall be used in a chemical fume hood.

When necessary, consult section and laboratory Material Safety Data Sheets (MSDS) regarding any chemical used in the Microanalysis section.

Label all generated solutions and reagents with appropriate warning stickers.

4.7. Limitations

Burned material from which a sample has been extracted usually contributes extraneous components. The presence of these extraneous product components is acceptable when sufficient ignitable liquid product compounds remain to allow proper classification of the sample. When the ignitable liquid pattern becomes overwhelmed by extraneous components, identification is not possible.

Extracts that meet the criteria for heavy petroleum distillates should be reviewed carefully to determine whether "extraneous components" that are the result of polyolefin or high molecular weight hydrocarbon (asphalt) decomposition are present.

The unexplainable absence of components from the middle of a pattern is generally sufficient grounds for a negative finding.

The presence of small quantities of some components common to a particular class of ignitable liquid product does not necessarily indicate the presence of that liquid in the debris.

Certain ignitable liquid components may be found in some substrates common to fire scenes, such as linoleum, carbonless paper forms, printed materials, adhesives and coatings, shoes, etc.

The examiner will use caution in interpretation of analytical results in these cases.

4.8. Procedure

Document submitted samples according to *Microanalysis Quality Assurance Policy*.

Evidence submitted may be photographed for case file documentation.

Document the evidence in the case by filling out a Fire Debris Worksheet for each exhibit or writing the case information on paper.

Based upon the evidence descriptions and case details, determine which recovery method is most appropriate for the submitted evidence. Document recovery method in case notes:

Headspace recovery is used for samples suspected of containing light, highly volatile solvents such as toluene, alcohols, and acetone. This technique may not be suitable for samples containing heavy, less volatile components. The technique may not produce reproducible results due to variables in the sample condition prior to headspace sampling. This is the least sensitive of the techniques.
Solvent extraction may be used for large items that will not fit into metal paint cans or nonporous items such as glass and metal containers. This technique may be hampered by the coincident extraction of interfering compounds present in the fire debris samples. This technique may not be useful for extracting light range products, which may evaporate during concentration.
Static adsorption elution recovery for all debris in sealed airtight cans and glass jars.

Direct injection of submitted liquid samples.

Open an air-tight container of evidence one at a time under a hood to prevent cross contamination and document contents in case notes.

If the air-tight container is full, contents may be placed in a larger container or split into multiple containers for analysis.

If there is further packaging inside the air-tight container, the packaging may be removed during analysis to prevent extraction of packaging materials.

If collection items, such as gloves, are inside the air-tight container, these may be removed during analysis to prevent extraction of these materials.

Document these activities in the case notes.

4.8.1. **Headspace Recovery**

Puncture a hole in the top of the air-tight container and place tape across the hole to prevent loss of any solvent and/or ignitable liquid that may be present.

Heat oven to 60°C - 80°C. Record oven temperature in case notes.

Place the air-tight container in the oven and heat for approximately an hour or for an appropriate amount of time depending on the amount of sample existing within the container. Only one case may be placed in an oven at a time.

Remove the air-tight container from the oven and extract a vapor sample through the hole at the top of the container with a headspace syringe. Record the length of time in the oven and sample volume in case notes

Prepare instrument for analysis using instrumental method "Headspace.m". Instrument parameters are retained as method files on the instrument computer and are electronically attached to each data file. Following are the critical parameters for this analysis.

Oven Temperatures

Initial temp	40°C
Initial time	3.0 min
Ramp rate	20°C/min
Final temp	100°C

Gas Type
Helium
Column Type
100% methylsilicone or 5% phenyl methylsilicone stationary phase

Length	20-30m
Internal diameter	0.2-0.25mm
Film thickness	0.1-0.5µm

Mass Spectrometer Parameters

Autotune file	atune.u
Mode	Scan
Solvent Delay	0.00min
Low Mass	10 amu
High Mass	100amu
MS Quad temp	150°C
MS Source temp	230°C

A solvent blank shall be analyzed prior to analyzing each sample. A known comparable solvent/ignitable liquid shall be successfully analyzed with each case.

4.8.2. **Solvent Wash Recovery**

If the item to be solvent washed can be divided, only a portion of the item should be extracted. A description and/or photograph of the extracted item should be included in the case notes.

Place the item over or in a clean beaker or tray free of extractable hydrocarbons and wash with carbon disulfide under a hood. When the inside of the container is to be analyzed, the carbon disulfide is placed inside, capped, swirled, and allowed to set. CAUTION: Vapors may cause the lids on the container to pop off, sometimes explosively. Slowly open lids to release pressure. Record the amount of carbon disulfide used in case notes.

Collect the liquid and evaporate to an appropriately small volume under a hood. Record the final volume in case notes.

Place concentrate into an appropriately labeled vial or bottle.

Prepare instrument for analysis using instrumental method “Arson.m”. Instrument parameters are retained as method files on the instrument

computer and are electronically attached to each data file. Following are the critical parameters for this analysis.

Oven Temperatures

Initial temp	40°C
Initial time	2.0 min
Ramp rate	15°C/min
Final temp	270°C
Hold time	2.5 min

Gas Type

Helium

Column Type

100% methylsilicone or 5% phenyl methylsilicone stationary phase

Length	20-30m
Internal diameter	0.2-0.25mm
Film thickness	0.1-0.5µm

Mass Spectrometer Parameters

Autotune file	atune.u
Mode	Scan
Solvent	Delay0.00min
Low Mass	30 amu
High Mass	350amu
MS Quad temp	150°C
MS Source temp	230°C

Injection

Volume 1.0 µL

A solvent blank shall be analyzed prior to analyzing each sample. The ASTM test mixture shall also be analyzed with each case. All data generated during the analysis shall be retained in the case file.

4.8.3. **Static Adsorption Elution Recovery**

Remove the carbon strip from the container. Using clean tweezers and razor blade, carefully cut the charcoal strip into four (4) equal sections.

Place one (1) piece of the carbon strip on a clean paper clip and attach the paper clip to a clean piece of string.

Open one air-tight container at a time under a hood. Suspend the carbon strip inside the container of evidence.

To assure that the recovery process and oven is functioning properly; an aliquot of C_{22} solution is placed in unused clean quart paint can for each oven to be used. A carbon strip is introduced and this can is placed in the oven. This carbon strip is then analyzed in the same manner as submitted cases. The resulting data is maintained in the case file.

Heat ovens to 60°C - 80°C. Record the oven temperature, the date and time in case notes. Place container(s) in the oven(s) and heat for an appropriate amount of time depending on the amount of sample existing within the containers and the number of containers being heated in each oven (no less than 2 hours and no more than 24 hours). Only one case may be placed in an oven at one time.

Remove container(s) from oven(s) and let it/them cool. Record oven temperature, the date and time in case notes.

Remove the strip from each container and place in an individual auto sampler vial. Label the vial with sample information.

Elute strip with a sufficient amount of carbon disulfide to cover the carbon strip. Record the date in case notes.

Double check all numbers on all vials.

Document the following in case notes (if not using the Fire Debris Worksheet):
- Adsorbent Type
- Adsorbent Amount
- Type of Elution Solvent
- Volume of Elution Solvent

Auto Sample Run – The ASTM test mixture must be analyzed at the beginning and end of each auto sample run to ensure the system is performing properly. These chromatograms shall be maintained in the case file.

Blanks shall be analyzed before each sample to ensure there is no carryover on the column of the Gas Chromatograph/Mass Spectrometer.

If contamination from the prior sample occurs, the sample shall be diluted and reanalyzed.

Prepare instrument for analysis using the instrumental method "Arson.m". Instrument parameters are retained as method files on the instrument computer and are electronically attached to each data file. Following are the critical parameters for this analysis.

Oven Temperatures

Initial temp	40°C
Initial time	2.0 min
Ramp rate	15°C/min
Final temp	270°C
Hold time	2.5 min

Gas Type

Helium

Column Type

100% methylsilicone or 5% phenyl methylsilicone stationary phase

Length	20-30m
Internal diameter	0.2-0.25mm
Film thickness	0.1-0.5µm

Mass Spectrometer Parameters

Autotune file	atune.u
Mode	Scan
Solvent Delay	0.00min
Low Mass	30 amu
High Mass	350amu
MS Quad temp	150°C
MS Source temp	230°C

Injection

Volume 1.0 µL

Create auto sample sequence using instrument software. The sequence shall contain all GC checks, blanks, and samples in the order they are to be analyzed.

Place vials into auto sampler tray and check to ensure they are in the same order as listed in the sequence. Document this check in case notes. Also document in case notes that blank vials, wash bottles and ASTM test mixture vial have been checked. Save sequence and begin the analysis run.

Once the run is completed, re-check the sequence order of the sample vials and document in case notes. Ignitable liquid residues present in the elution solvent may be re-adsorbed onto the carbon strip and should remain stable indefinitely.

4.8.4. **Direct Injection**

Place a small aliquot of the liquid sample into an auto sampler vial and dilute with carbon disulfide. Record the amount of liquid and the amount of carbon disulfide used in case notes.

This sample vial may be included in an auto sample sequence and analyzed as above.

If the sample is to be hand-injected, prepare the instrument using the parameters listed above and inject 1 µL of sample.
A solvent blank shall be analyzed prior to analyzing each sample. The ASTM test mixture shall be analyzed with each case. All data generated during the analysis shall be retained in the case file.

4.9. Interpretation

The data produced by the Gas Chromatograph/Mass Spectrometer is subject to a computer program that generates a Total Ion Chromatogram (TIC) and Extracted Ion Chromatograms (EIC) for alkanes, aromatics, cycloparaffins, dihydroindenes, naphthalenes and terpenes. The following ions shall be used for the different EICs: Alkanes (57, 71, 85, 99), Cycloparaffins (55, 69, 83, 97), Aromatics (91, 105, 119, 134), Naphthalenes (128, 142, 156, 165), Dihydroindenes (117, 131, 145, 159), Terpenes (68, 93, 121,136). The TIC and EICs are compared to known standards for interpretation. Copies of known standard TIC and EICs shall be placed in the case file when a classification is made. A minimum of three mass spectra of individual peaks shall be compared to mass spectra of known compounds (i.e. library search). These mass spectra shall be placed in the case file. Peak identifications may provide additional information for classification. Classification is based on the classification system outlined below. The number of mass spectra created for a negative sample is left to the analyst's discretion.

Minimum Criteria for Classifying an Unknown Pattern

4.9.1. Gasoline

The general pattern is characterized by abundant aromatics in a specific pattern.
Alkanes are present. Pattern may vary by brand, grade, and lot.
Cycloparaffins are not present in significant amounts.
Aromatics pattern is comparable to that of the reference ignitable liquids. 1-methyl-3-ethylbenzene, 1-methyl-4-ethylbenzene, 1,3,5-trimethylbenzene, 1-methyl-2-ethylbenzene, and 1,2,4-trimethylbenzene must be present.
Condensed Ring Aromatic patterns are comparable to that of the reference ignitable liquids. Naphthalene, 1- and 2-methylnaphthalene are usually present. These compounds may be absent in some gasoline. Indan and methyl indans are usually present.

4.9.2. Distillates

General pattern is typified by a Gaussian distribution of peaks with aromatic compounds present.
Alkanes are abundant. Predominant n-alkanes in normal distribution, saturated branched alkanes must be present.
Cycloparaffins are present, but less abundant that alkanes.
Aromatics are always present in medium and heavy distillates, and may be present in light distillates. They are less abundant than alkanes and vary by boiling range and peak spread.
Condensed Ring Aromatics may be present.
Light Distillate has a majority of the pattern occurring in the range C_4-C_9 and no major peaks associated with the ignitable liquid exist above C_{11}.
Medium Distillate has a majority of the pattern occurring in the range C_8-C_{13} and no major peaks associated with the ignitable liquid below C_7 or above C_{14}. These are typically narrow range products.
Heavy Distillates are typically broad range products with the majority of the pattern occurring in the range C_9-C_{23} with a continuous pattern spanning at least 5 consecutive n-alkanes. Also included in the class are narrow range (encompassing less than five n-alkanes) ignitable liquid products starting above C_{11}.

4.9.3. Isoparaffinic Products

This product is comprised almost exclusively of branched chain aliphatic compounds (isoparaffins). The boiling range and pattern are dependent on the specific formulation.
Alkanes are abundant. Pattern is comparable to known isoparaffinic formulation. Characteristic isoparaffin product patterns are present with no or insignificant levels of n-alkanes.
Aromatics are absent or not present in significant concentrations.

Cycloparaffins are absent or not present in significant concentrations.
Condensed Ring Aromatics are not present.

4.9.4. Aromatic Solvents

This product is comprised almost exclusively of aromatic and/or condensed ring aromatic compounds. The boiling range and pattern are dependent on the specific formulation.
Alkanes are not present in significant amounts.
Cycloparaffins are not present in significant amounts.
Aromatics are abundant. Pattern is comparable to known aromatic products.
Condensed Ring Aromatics may be present. Pattern depends on formulation and is comparable to known aromatic products.

4.9.5. Naphthenic-Paraffinic Solvents

This product is comprised mainly of branched chain (isoparaffinic) and cyclic (naphthenic) alkanes. The boiling range and pattern are dependent on the specific formulation.
Alkanes are abundant. Normal alkanes may be notably absent or diminished. Patterns are comparable to known naphthenic-paraffinic products.
Cycloalkanes are abundant and pattern is comparable to known products.
Aromatics are not present in significant amounts.
Condensed Ring Aromatics are not present in significant amounts.

4.9.6. Normal Alkanes

This product is comprised exclusively of n-alkanes. The boiling range and pattern are dependent on the specific formulation.
Normal alkane product pattern is present with no isoparaffins or only minor levels of isoparaffins.
Cycloalkanes are not present in significant amounts.
Aromatics are not present in significant amounts.
Condensed Ring Aromatics are not present in significant amounts.

4.9.7. Oxygenated Products

These solvents contain oxygenated components or a mixture of oxygenated compounds and other compounds or products. Oxygenated compounds should be present before C_8 and may include alcohols, esters, or ketones. Other compounds or products found in mixtures may include toluene, xylene, and distillate formulations.

There should be a large excess of the compound (at least one order of magnitude above the other peaks in the chromatogram) before the analyst should consider the finding of an oxygenated product significant.

5. Measurement Traceability

Ignitable liquid examinations and comparisons are qualitative techniques and as such do not utilize measurements that will have a significant effect on the outcome of the analysis.

6. Reference Materials

A reference collection of various ignitable liquid samples will be maintained in the Microanalysis section. This collection will be used for classification, training and interpretation purposes. The collection generally will be in the form of small quantities of liquids. The samples will be identified and documented. The collection shall be maintained in a location that protects it from contamination and alteration.

ASTM 1618 Column Resolution Test Mixture

7. Reports

The following are possible results concluded from the examination:

Analysis of this exhibit did not reveal the presence of any ignitable liquid residue. This result does not eliminate the possibility that an ignitable liquid was used. (AC1)

Analysis of this exhibit revealed the presence of **gasoline**. This result includes all brands and grades of automotive fuels. (AC2)

Analysis of this exhibit revealed the presence of **evaporated gasoline**. This result includes all brands and grades of automotive fuels. (AC3)

Analysis of this exhibit revealed the presence of a **light petroleum distillate**. Products in this range include, but are not limited to: cigarette lighter fluids, solvents for glues, adhesives and cleaners, V M & P naphtha, some camping fuels and some aviation gasolines. (AC4)

Analysis of this exhibit revealed the presence of a **medium petroleum distillate**. Products in this range include, but are not limited to: mineral spirits, some paint thinners, some charcoal starters, “dry cleaning” solvents, some torch fuels, some solvents for insecticides and polishes, and some lamp oils. (AC5)

Analysis of this exhibit revealed the presence of a **heavy petroleum distillate**. Products in this range include, but are not limited to: kerosene, diesel fuel, fuel oils No. 1 and 2, Jet-A (aviation) fuel, some charcoal starters, some torch fuels, some paint thinners, some solvents for insecticides and polishes, and some lamp oils.(AC6)

Analysis of this exhibit revealed the presence of an **isoparaffin product**. Products in this range include, but are not limited to: some charcoal starters, some copier fluids, some aviation gasoline, some lamp oils, some solvents for insecticides and polishes and some camping fuels. (AC8)

Analysis of this exhibit revealed the presence of an **aromatic solvent**. Products in this range include, but are not limited to: some paint thinners, some insecticides, some fuel additives, and some cleaning solvents. (AC9)

Analysis of this exhibit revealed the presence of a **naphthenic/paraffinic solvent**. Products in this range include, but are not limited to: specialty solvents/fuel products, some lamp oils, some insecticides, and some charcoal starters. (AC10)

Analysis of this exhibit revealed the presence of a **normal alkane product**. Products in this range include, but are not limited to: some lamp oils, some solvents for insecticides and polishes, and other specialty products. (AC11)

Analysis of this exhibit revealed the presence of an **oxygenated product**. (Due to the variability of the products in this category the analyst will create a list of products specific to the case.) (AC13)

Analysis of this exhibit revealed the presence of **terpenes**, which are present in turpentine, scented cleaners and occur naturally in some wood products. (AC14)

Analysis revealed the presence of **toluene**. It should be noted that toluene may be used in the manufacturing of some shoes. (AC15)

Analysis of this exhibit was inconclusive. The results did not meet the criteria for identifying or classifying an ignitable liquid. (AC16)

The words “light”, “medium”, and “heavy” may be added to the isoparaffin, alkane, aromatic, naphthenic/paraffinic and oxygenated product results to further classify these products if desired.

The word “evaporated” may be added to further describe any classification.

A note may be added to results when a known background substrate could contain an ignitable liquid, i.e. shoes, flooring materials, carbonless paper forms, or adhesives.

Combinations of results may be made when a mixture of products are present in the sample.

The exact wording of the result may vary depending on the particular nature of an individual case.