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# OVERVIEW

## Summary of Test Methods

The following protocols for extractions and interpretation of ignitable liquids in fire debris evidence in the Alaska Department of Public Safety Scientific Crime Detection Laboratory use the following the latest ASTM International standards as reference guides:

- ASTM E1386 Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Solvent Extraction
- ASTM E1388 Standard Practice for Sampling of Headspace Vapors from Fire Debris Samples
- ASTM E1412 Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Activated Charcoal
- ASTM E1618 Standard Test Methods for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry
- ASTM E2451 Standard Practice for Preserving Ignitable Liquids and Ignitable Liquid Residue Extracts from Fire Debris Samples

This laboratory utilizes a gas chromatograph (GC) which is interfaced to a mass spectrometer (MS) with a data station (computer) capable of storing and handling chromatographic and mass spectral data.

Total ion chromatograms (TICs) and Extracted Ion Profiles (EIPs) are evaluated by visual pattern matching against reference ignitable liquids for the purpose of detecting and classifying ignitable liquids and residues. EIP data contains less interfering combustion and pyrolysis products, which are formed when materials are subjected to fire, and help indicate certain classes of compounds, as mentioned in ASTM E1618, and are included in Appendix B, **Table 7**.

## Significance and Use

The identification and classification of ignitable liquids or residues in evidence samples from a fire scene may assist the fire investigator regarding the origin, cause, and incendiary nature of the fire.

The identification and classification of ignitable liquids or residues in a fire scene does not necessarily lead to the conclusion that a fire was criminal in nature. Further investigation may reveal a legitimate reason for the presence of ignitable liquids or residues.

Due to the volatility of ignitable liquids and residues, and variations in sampling techniques, the absence of detectable quantities of ignitable liquids or residues does not necessarily lead to the conclusion that ignitable liquids or residues were not present at the fire scene.

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## INSTRUMENTATION, EQUIPMENT, MATERIALS

The minimum instrumentation, equipment and materials necessary for fire debris analysis are:

- Gas Chromatograph/Mass Spectrometer (GC/MS) designated as "Delta"
    - Gas Chromatograph (GC) with an Autosampler
    - GC capillary column is 100% Dimethylpolysiloxane, with dimensions ≈ 30m x 250µm x 0.25µm
    - Mass Spectrometer (MS) capable of scanning from 15 - 400 m/z
    - Computer and software able to control the GC and MS, retrieve mass spectral data and provide a library search
    - Helium, chromatography grade (99.999+ %)
- Reference Ignitable Liquid collection
- Preparatory Oven (~5 $ft^3$) is forced air
- Carbon Disulfide, HPLC grade
- Charcoal adsorption strips (C-strips), (from Albrayco Laboratories, Cromwell, CT)
- Supplies of coated metal paint cans with lids (quart and gallon), fire debris plastic bags, glass screw-top GC vials and inserts, caps, Dentotape® dental floss, disposable plastic pipets, new small metal paper clips, razor blades

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## QUALITY CONTROLS

Information and Data for Chemicals and Supplies are maintained in the "Fire Debris Quality Control Binder"

### Storage of Supplies

Carbon Disulfide, C-strips, coated metal paint cans with lids (quart and gallon), fire debris plastic bags, glass screw-top GC vials and inserts, caps, Dentotape® dental floss, disposable pipets, new small metal paper clips, and razor blades **must** be stored properly to ensure they are free of contamination and from extractable hydrocarbons

### GC/MS Calibration

The MS is tuned prior to the analysis of a sequence of samples.
Records are maintained in the "Fire Debris Instrument Logbook" located near the GC/MS, and annually archived into the LIMs.

### GC/MS Maintenance

The Gas Chromatograph and Mass Spectrometer are cleaned and maintained as needed (source, septa, liner, etc.). Records are maintained in the "Fire Debris Instrument Logbook" located near the GC/MS.

GC/MS Autosampler syringe is automatically rinsed between sample injections.

### Reference Ignitable Liquids

Various commercial, industrial, and retail chemicals or products that are flammable or combustible. These Reference Ignitable Liquids are stored in a solvent cabinet in the Solvent Room.

The data for these references are located in the "GC/MS Reference Ignitable Liquid Library" binder and on the Fire Debris GC/MS computer.

### OXY-SAM Solution (Oxygenated-Standard Accelerant Mixture)

At a minimum, an in-house OXY-SAM solution must be analyzed with each case or batch of cases to show the proper operation of the Gas Chromatograph, autosampler, syringe, GC liner, GC column, Mass Spectrometer, GC/MS computer, and the Extracted Ion Profile macro. {see Appendix B - **Table 1** – "OXY-SAM" solution" GC/MS Oxygenated-Standard Accelerant Mixture}

The STOCK and WORKING solutions must have lot numbers assigned to them.

The WORKING solution lot number is referenced when analyzing evidence samples.

**All** the STOCK and WORKING solutions must be stored in the refrigerator, and the WORKING OXY-SAM solution needs a new cap after use.

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## Test Mixture

A commercial product consisting of 13 chemicals must be analyzed approximately four times a year to show good resolution from the Gas Chromatograph, and good sensitivity from the Mass Spectrometer.

Records are maintained in the "Fire Debris Quality Control Binder" located near the GC/MS. E1618-97 Test Mixture (available from Restek, Bellefonte, PA)

## Container Blank

A Container Blank is either a "paint can" or a "fire debris plastic bag" that is new, empty and prepared in the same manner as the evidence samples, and analyzed with the evidence samples.

## Extraction Solvent

A new lot of an Extraction Solvent bottle is concentrated to ≈ 50:1, analyzed prior to evidence sample analysis, and the data is examined for significant contamination.

The extraction solvent is used as a "Reagent Blank", and is analyzed just prior to the analysis of each evidence sample, and recorded along with the evidence sample in the case file.

If significant contamination is present, it must be alleviated prior to further analysis of evidence samples, and documented in the "Fire Debris Quality Control Binder" located near the GC/MS.

## C-strips

A new lot of C-strips are analyzed by GC/MS:

- By placing a ¼ of a C-strip in a GC vial with insert, containing $CS_2$ for contamination testing, and,
- By placing a ¼ of a C-strip into a formerly analyzed, empty metal quart paint can containing two drops of 100% Gasoline onto a small Kimwipe® to verify the C-strip efficiency

If contamination is present, the analysis must be repeated.

If contamination is still present, the C-strip manufacturer must be contacted to resolve the issue.

The quality control analysis of C-strips is documented in the "Fire Debris Quality Control Binder" located near the GC/MS.

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## Preparatory Oven

The oven temperature is set at 65 °C +/- 2 °C and the temperature is recorded in the “Oven Logbook”, before evidence containers are placed inside the oven and when the evidence containers are removed from the oven.

## GC/MS Data

Every case file must include the Total Ion Chromatogram (TIC), the Extracted Ion Profile (EIP) from the macro program for every evidence sample, and at least one appropriate Reference Ignitable Liquid.

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## SEPARATION & CONCENTRATION PROCEDURES

### Passive Headspace Concentration with Activated Charcoal

This procedure is used for sampling ignitable liquid residue from samples of fire debris. The method is nondestructive. the method is used for fire debris evidence packaged in airtight containers, such as metal paint cans or fire debris bags. Passive Headspace (PHS) Concentration may not distinguish between #1 and #2 Fuel Oils, waxes, vegetable oils, engine oils, bunker oils, lubricating oils, etc. It may not detect ignitable liquid residue very low in concentration.

1) Briefly open and examine the fire debris sample in order to determine that it is consistent with its description. Resolve any discrepancies.

2) Place a two C-strips on the end of a new and clean small paper clip and suspend in the evidence container. The paper clip may be attached to the inside of the lid by use of a magnet or hung in the can by a piece of dental floss.

3) Reseal the container and place in an oven set to **≈ 65** °C for **≈ 18** hours. The adsorption temperature and duration may vary based on the evidence sample.

4) **CAUTIONARY NOTE:** When other evidentiary considerations arise, such as document or latent print examinations, it may be appropriate to conduct the adsorption at room temperature for extended periods, such as **24** hours or longer, to minimize damage or to detect low molecular weight compounds.

5) After heating, the container is removed from the oven and allowed to cool to room temperature.

6) The C-strips are removed from the container. One C-strip is placed in a labeled vial and returned with the evidence. The other C-strip is placed into a labeled GC vial with insert. Carbon disulfide is added to the GC vial insert and sealed with a screw cap. The sample is now ready for GC/MS analysis.

7) A parameter sheet must be included in the case file and contain the following information: lot numbers of the C-strips and extraction solvent, the size of the C-strip, the volume of extraction solvent, the oven temperature, the approximate time in the oven, and the GC/MS column and parameters.

{see Appendix B - **Table 2** – Parameter Sheet example}

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## Solvent Extraction

Due to size and/or packaging, certain evidence samples may not be suited for using the Passive Headspace Concentration technique. This method is useful for extracting ignitable liquid residues from very small or very large non-porous containers. It is also useful when attempting to distinguish between various grades of Fuel Oils, since it extracts low volatile compounds.

1) Open and examine the fire debris sample in order to determine that it is consistent with its description. Resolve any discrepancies.
2) Place a representative sample in a clean beaker.
3) Thoroughly moisten and mix the sample with a sufficient volume of solvent such as $CS_2$.
4) For some items of evidence (such as fuel containers) the $CS_2$ may be added directly to rinse any ignitable liquid residues.
5) Decant the $CS_2$ into a second clean beaker and filter if necessary.
6) Reduce the $CS_2$ volume in a hood by allowing it to evaporate to ≈ 1 mL to concentrate any ignitable liquid residues that may be present.

   **NOTE**: DO Not Evaporate To Dryness **!!**

7) The sample is then transferred to a GC vial for GC/MS analysis.
8) Return the $CS_2$ extract with the evidence by inserting C-strips in the GC vial to absorb as much of the $CS_2$.

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## Sampling of Headspace Vapors

This method may be employed when the investigator suspects that a light oxygenate may be present, and strong odor of alcohol is detected.

This practice is the least sensitive of the sample preparation techniques and may not detect quantities of less than 10 µL of petroleum product. Because this separation takes place in a closed container, the sample remains in approximately the same condition in which it was submitted. Due to inconsistencies in the debris sample condition, reproducibility of TICs may be difficult to obtain. High concentrations of highly volatile compounds may overwhelm the headspace, inhibiting the recovery of less volatile compounds.

1) Open and examine the fire debris evidence in order to determine that it is consistent with its description. Resolve any discrepancies.
2) A gas-tight syringe Air Blank consisting of air is analyzed on the GC/MS using an appropriate method by not shutting off the filament.
3) Punch a small hole in the lid of the paint can with a tool such as a nail and immediately place a piece of transparent adhesive tape over the hole.
4) Analyze an ambient sampling first, and then place the can in an oven at ≈ 65 °C for ≈ 30 minutes.
5) Insert the syringe needle through the taped hole, pump it several times, and withdraw ≈ 1 mL of headspace. Inject into the GC/MS using an appropriate GC/MS method.
6) Reseal the hole with tape.
7) Re-analyze the evidence container using the Passive Headspace Concentration technique.

## Sampling Liquid Samples

1) Check the pH of the liquid
2) The liquid sample may be analyzed by a flame test. This is accomplished by placing a few drops of the liquid into a small aluminum pan and gently exposing the liquid to a flame
3) Test the miscibility of the liquid with water, if the liquid does not ignite
4) An aqueous sample may be extracted by liquid-liquid extraction with $CS_2$

The results of these tests are documented in the bench notes.

**NOTE**: Clean organic evidence samples **must** be diluted with $CS_2$ before GC/MS analysis. Typically, a dilution is 1 drop/mL $CS_2$

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## GC/MS ANALYSIS

After GC/MS analysis of the evidence samples, the TIC, EIP, and mass spectral data are evaluated by comparison to reference ignitable liquid data.

Evidence samples and a reference ignitable liquid must be analyzed using the same GC/MS method within 30 days.

The GC/MS utilizes an autosampler for injecting evidence samples and reference ignitable liquids, which is controlled by a “sequence” procedure. {see Appendix B - **Table 3** - Sequence Table Setup}

All the GC/MS methods are printed and placed in the “Fire Debris Instrument Logbook” located near the GC/MS.

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## DATA ANALYSIS

1) Access to data:
   - On the GC/MS computer, “Enhanced Data Analysis”, “File”
   - “Load Data File…”, change path, select data file, TIC in upper window
   - For a 2-page TIC and EIP report, type <macro “deltaakaion”,go> {see Appendix B, **Table 4**, for EIP macro command information}
   - To obtain the Mass Spectrum of a TIC peak, widen peak, double right click on the peak center, mass spectrum appears in lower window
   - For a library search of a peak, double right click on the mass spectrum, “Search Results” are at bottom of screen
2) The carbon number range is determined by comparing the TIC of the evidence sample to the OXY-SAM solution, Test Mixture, or to similar products containing known n-alkanes
3) Extracted Ion Profiles for chemical families must be used to enhance the signal-to-noise ratios and to decrease the influence of interfering compounds {see Appendix B, **Table 5,** and **Table 6** – Additional Chemical Families & Extracted Ions}
4) An identification of an ignitable liquid is made by a combination of:
   - Visual pattern matching of TICs with reference ignitable liquids
     - Relative retention times
     - Relative ratios to each other
   - Visual pattern matching of EIPs with reference ignitable liquids
     - Relative retention times
     - Relative ratios to each other
   - Mass Spectral library search of significant peaks
     - Major peaks
     - Minor peaks
     - Unusual grouped peaks
     - Unusual located peaks
   - Visual pattern matching of TICs and EIPs can be assisted by:
     - In-house “GC/MS Reference Ignitable Liquid Library”
     - “NCFS – Ignitable Liquids Reference Collection”
     - Authoritative forensic books and Journal papers

       **NOTE**: These libraries are only intended to give guidance for selection of reference ignitable liquids

**NOTE**: If the evidence sample EIP seems to indicate a close comparison to a reference ignitable liquid EIP, but the evidence sample TIC pattern is too obscured as compared to the reference ignitable liquid, then the positive comparison is negated.
The ignitable liquid TIC pattern must be visible in the evidence sample TIC

5) Raw data files are retained for technical review

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## INTERPRETATION

Ignitable liquids consist of compounds in different chemical families, which have been organized into the following classification system, based on ASTM E1618 (see Appendix B, **Table 7**)

The significant compounds that comprise ignitable liquids consist of:

- Alkanes (both normal and branched)
- Alkenes
- Cycloparaffins
- Aromatics
- Naphthalenes
- Indanes
- Oxygenates

➢ Distinguishing between examples within a classification may be possible, but not consistent.

➢ The ignitable liquids listed in Appendix B **Table 7** for the various classifications are illustrations of known commercial uses. These examples are not intended to be all-inclusive.

➢ Some ignitable liquids are found in multiple classifications, such as "charcoal starters." Therefore, many of the examples must be prefaced by the word "some," as in "some charcoal starters."

1) With the exception of the gasoline classification, the major ignitable liquid classes may be divided into 3 subclasses based on boiling range: Light, Medium and Heavy.
2) Light product range: n-$C_4$ – n-$C_9$, the majority of the pattern occurs in the range n-$C_4$ – n-$C_9$, no major peaks exist above n-$C_{11}$.
3) Medium product range: n-$C_8$ – n-$C_{13}$, narrow range products, the majority of the pattern occurs in the range n-$C_8$ – n-$C_{13}$, no major peaks below n-$C_7$ or above n-$C_{14}$.
4) Heavy product range: n-$C_9$ – n-$C_{20}$, typically broad range products, the majority of the pattern occurs in the range n-$C_9$ – n-$C_{20}$, with a continuous pattern spanning at least 5 consecutive normal hydrocarbons, or ignitable liquid products starting above n-$C_{11}$.
5) It may be necessary to characterize a product as "light to medium," or "medium to heavy," when the carbon number range does not fit neatly into one of the above categories. In such instances, the carbon number range should be reported.

## Ignitable Liquid Classification

**In order for an ignitable liquid to be classified, the following minimum criteria must be met:**

## Criteria for the Classification of Gasoline

GENERAL: All brands of gasoline including gasohol and E85. Pattern characterized by abundant aromatics in a specific pattern.

ALKANES: Present. Pattern may vary by brand, grade, and lot.

CYCLOALKANES: Not present in significant amounts.

AROMATICS: Petroleum pattern comparable to that of reference ignitable liquids; 1-methyl-3-ethylbenzene (m-ethyltoluene), 1-methyl-4-ethylbenzene (*p*-ethyltoluene), 1,3,5-trimethylbenzene, 1-methyl-2-ethylbenzene (*o*-ethyltoluene), and 1,2,4-trimethylbenzene) must be present; above n-$C_7$, the aromatic concentration is generally substantially higher than the alkane concentration.

CONDENSED RING AROMATICS: Pattern comparable to known reference ignitable liquids is usually present, including naphthalene, 1- and 2-methylnaphthalenes. These compounds may be absent in some gasolines. Indan (dihydroindene) and methyl indans are usually present.

**WARNING**: The mere presence of alkylbenzenes does not justify an identification of gasoline. These compounds must be present at approximately the same relative concentrations as are observed in samples of known gasoline. Many carpet samples that have been exposed to fire conditions contain these compounds in some concentrations. Benzene, toluene, ethylbenzene, xylenes, cumenes, ethyltoluenes, and naphthalenes, which are present in gasoline, are also sometimes found in fire debris samples containing no foreign ignitable liquid residues. The presence of high levels of alkenes and oxygenates may indicate significant pyrolysis of the matrix and should make the recovery suspect. The presence of high levels of aromatics without the appropriate levels of alkanes may indicate an aromatic product.

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## Criteria for the Classification of Distillates

GENERAL: Traditional distillates and de-aromatized distillates; Predominant pattern associated with a homologous series of n-alkanes in a Gaussian distribution of peaks. Light distillates may not exhibit a recognizable pattern and may contain one or two of the n-alkanes.

ALKANES: Abundant. Predominant n-alkanes present with isoparaffinic compounds present.

CYCLOALKANES: Present, less abundant than alkanes. Pattern varies by boiling range and peak spread.

AROMATICS: Always present in traditional medium and heavy distillates; less abundant than alkanes; pattern and abundance varies by boiling range and peak spread; may be present in light distillates. In some products, the aromatic composition may be significantly reduced or completely absent (de-aromatized).

CONDENSED RING AROMATICS: May be present based on boiling range and peak spread.

## Criteria for the Classification of Isoparaffinic Products

GENERAL: Product comprised almost exclusively of branched chain aliphatic compounds (isoparaffins). The boiling range and pattern are dependent on the specific formulation.

ALKANES: Abundant. Pattern comparable to known isoparaffinic formulation. Characteristic isoparaffin product patterns present with no or insignificant levels of n-alkanes. The boiling range and compound pattern are dependent on the specific formulation.

AROMATICS: Absent, or not present in significant concentrations.

CYCLOALKANES: Absent, or not present in significant concentrations.

**NOTE**: Ions indicative of cycloparaffins are also present in smaller amounts in isoparaffinic compounds. “Cycloalkane” pattern representing isoparaffins may be present, but significantly less abundant than the alkane pattern.

CONDENSED RING AROMATICS: Not present.

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## Criteria for the Classification of Aromatic Products

GENERAL: Products comprised almost exclusively of aromatic or condensed ring aromatic compounds, or both. The boiling range and pattern are dependent on the specific formulation.

ALKANES: Not present in significant amounts.

CYCLOALKANES: Not present in significant amounts.

AROMATICS: Abundant. Pattern comparable to known aromatic products. Pattern depends on formulation.

CONDENSED RING AROMATICS: May be present, pattern depends on formulation. Pattern comparable to known aromatic product.

**NOTE**: Light aromatic products may consist of single or a few compounds. These compounds must be identified by both GC retention time and mass spectral identification**.**

**WARNING** – The relative intragroup ratios of the isomers of xylenes and $C_3$-alkylbenzenes do not vary significantly among petroleum products. Therefore, the relative ratios of these compounds should match, or nearly match, the ratios found in petroleum products, if they are to be reported. Further, in the presence of Styrene at a concentration significantly higher than that of Toluene or Xylenes, the finding of Toluene or Xylenes should not be considered significant.

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## Criteria for the Classification of Naphthenic-Paraffinic Products

GENERAL: Products comprised mainly of branched chain (isoparaffinic) and cyclic (naphthenic) alkanes. The boiling range and pattern are dependent on the specific formulation.

ALKANES: Abundant. Branched alkanes present while n-alkanes may be notably absent or at diminished levels compared to distillate products. Pattern comparable to known naphthenic-paraffinic products.

CYCLOALKANES: Abundant. Pattern comparable to known naphthenic-paraffinic products.

AROMATICS: Not present in significant amounts.

CONDENSED RING AROMATICS: Not present in significant amounts.

## Criteria for the Classification of Normal Alkane Products

GENERAL: Product comprised exclusively of n-alkanes. The boiling range and pattern are dependent on the specific formulation.

ALKANES: N-alkane product pattern present with no isoparaffins or only minor levels of isoparaffins. The boiling range and pattern are dependent on the specific formulation.

CYCLOALKANES: Not present in significant amounts.

AROMATICS: Not present in significant amounts.

CONDENSED RING AROMATICS: Not present in significant amounts.

**NOTE**: All major chromatographic peaks for this class must be identified by both GC retention time and mass spectral characteristics.

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## Criteria for the Classification of Oxygenated Solvents

GENERAL: Products containing major oxygenated compounds may include mixtures of oxygenated compounds and other compounds or products. Major oxygenated compounds present before $C_8$; major compound(s) may include Alcohols, Esters, and Ketones. Other major compounds including Toluene, Xylene, and distillate formulations may also be present.

ALKANES: If in a mixture, may contain characteristic petroleum distillate pattern; pattern depends on formulation.

CYCLOALKANES: Pattern depends on formulation.

AROMATICS: Pattern depends on formulation.

CONDENSED RING AROMATICS: Not significant.

**NOTE**: All major oxygenated compounds must be identified by GC retention times and mass spectral characteristics.

**WARNING**: The mere presence of oxygenated solvents such as Alcohols or Acetone does not necessarily indicate that a foreign ignitable liquid is present in the sample. There should be a large excess of the compound (at least one order of magnitude above the matrix peaks in the TIC) before the analyst should consider the finding of an oxygenated product significant.

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## Criteria for Classification of Miscellaneous/Other

No classification system is likely to describe all possible ignitable liquids.

Numerous commercial and industrial products that are ignitable may fall into more than one classification or do not fall into any of the above classifications other than Miscellaneous/Other.

Many of these synthetic mixtures consisting of only a few compounds, rather than distillation, require GC retention times and mass spectra of the compounds in order to achieve classification.

## Factors Affecting Interpretation of Results

Pattern matching of EIPs rarely gives perfect correlation with reference ignitable liquids. In general, the unknown pattern (if positive) will be skewed toward less volatile compounds for weathered samples, or skewed towards more volatile compounds for incompletely recovered samples. Compounds may be missing from the light end, the heavy end, or both. Under certain conditions, selective loss of chemical families may result from microbiological degradation. Compounds may also be added to the pattern when the pyrolysis or combustion of materials at the fire scene yields compounds of the same chemical families as those being compared. All of these circumstances must be taken into account by the analyst during visual pattern evaluation. Therefore, it is imperative that the analyst have a sufficient library of reference ignitable liquids, in successive stages of evaporation. A library of extracts from common substrate materials containing no foreign ignitable liquids should also be maintained.

## Interferences

***Extraneous Compounds***-Burned material from which the sample has been extracted usually contributes extraneous compounds to an extract.

The amount and type of pyrolysis and combustion products formed during a fire depend on the substrate material and its fire history.

They can consist of Oxygenated compounds, Paraffinic, Cycloparaffinic, Aromatic, or Condensed Ring Aromatics, all of which will appear in the EIPs.

Extracts that meet the criteria for Heavy Petroleum Distillates should be reviewed carefully for "extraneous compounds" that elute near n-alkanes and are the result of Polyolefin or high molecular weight hydrocarbon (asphalt) decomposition.

Peaks representing the corresponding 1-alkene or 1, (n-1)-diene, and having a concentration near the concentration (within ½ an order of magnitude) of the alkane, should be considered as indicating the presence of Polyolefin products or asphalt decomposition products rather than Fuel Oil products.

Polyolefin decomposition products typically do not exhibit the same pattern of branched alkanes as Fuel Oils.

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***Missing Compounds***-Exposure of the ignitable liquid to heat usually results in the preferential loss of lighter compounds, thereby enhancing the chromatographic pattern at the heavy end. Some sample preparation techniques may result in the preferential recovery of either the lighter or the heavier compounds, resulting in the "loss" in the opposite end. Neither of these factors will cause the selective loss of intermediate compounds. The unexplainable absence of compounds from the middle of a pattern is generally sufficient grounds for a negative finding. Possible explanations for missing intermediate compounds include low sample concentration (compound below detection limit), distortion of the mass spectrum by a co-eluting extraneous compound, and, in rare cases, selective loss due to digestion by microbes. Any such explanation for loss of compounds in the middle of a pattern must be scientifically supportable, and efforts should be made, if possible, to retrieve evidence of their existence from the data file or by reanalyzing the sample.

The presence of small quantities of some compounds common to a particular class of ignitable liquid product does not necessarily indicate the presence of that liquid in the debris at the time of the fire. For example, the pyrolyzates of some polymers may include Toluene and Xylenes. The pyrolyzates of polyolefin plastic may include a homologous series of n-alkanes.

Certain ignitable liquid compounds may be found in some substrates common to fire scenes. For examples, n-alkane products found in linoleum and in carbonless paper forms; distillates found in some printed materials; and solvents used in some adhesives and coatings.

If there is suspicion that an ignitable liquid found might be indigenous to the substrate, the testing of an appropriate comparison sample, if available, may aid in determining whether an ignitable liquid is foreign to the substrate.

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## Case Bench Notes

- A detailed description of each item of evidence and its packaging
- An updated "Parameter Sheet" (see Appendix B, **Table 2**)
- Extraction method used (e.g. passive headspace) for each item
- TIC and EIP for each:
  - evidence sample
  - Reference Ignitable Liquid used for comparison
- TIC of each:
  - empty Container Blank
  - Reagent Blanks prior to evidence sample analysis
- Conclusions reached from analysis
- Disposition of adsorbed but unused C-strips
- Dates that analysis began and was completed

## LIMS Case File

- Request for Laboratory Services
- Complete chain of custody information for all evidence
- When generated from LIMS, the case file pages are numbered and the final page is indicated.

## REPORTS

- Laboratory number
- Agency case number
- Submitting Agency
- Name of person receiving report
- Item numbers
- Item descriptions
- "Results, Conclusions and Opinions" is the analyst's opinion based on all the GC/MS data

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# APPENDIX A

## Abbreviations

≈: approximately

ASTM: ASTM International

$C_x$ : x is the number of carbons

HPD: Heavy Petroleum Distillate

LPD: Light Petroleum Distillate

MPD: Medium Petroleum Distillate

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# Appendix B

## Table 1

"OXY-SAM Solution"

GC/MS Oxygenated-Standard Accelerant Mixture

An OXY-SAM solution must be analyzed with each case or batch of cases to show the proper operation of the Gas Chromatograph, autosampler, syringe, GC liner, GC column, Mass Spectrometer, Data Station, and the Extracted Ion Profile macro.

**STOCK** SAM solution consists approximately of:

- Gasoline (JRG-104) 10 drops
- Jet A (JRG-086) 20 drops
- Diesel Fuel (JRG-107) 20 drops

(50 drops ~ 0.94 mL in a 2 mL vial)

**STOCK** OXY-MIX solution consists approximately of:

- Methyl Alcohol 10 drops
- Ethyl Alcohol 10 drops
- Acetone 10 drops
- Isopropyl Alcohol 10 drops
- Methyl Ethyl Ketone 10 drops
- Methyl Isobutyl Ketone 10 drops

(60 drops ~ 1.1 mL in a 2 mL vial)

**WORKING** OXY-SAM solution consists approximately of:

1 drop of STOCK OXY-MIX solution + 2 drops STOCK SAM Mixture in 2 mL $CS_2$

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## Appendix B - Table 2 - Parameter Sheet example

**Alaska Scientific Crime Detection Laboratory #: 14-09876**
**Date: September 1, 2014**

Analyst Name, Forensic Scientist III

**Equipment and Parameters Summary Sheet**

### Instrument and Operating Parameters

Method name: ARSON

Gas Chromatograph (Agilent® 7890A)

| | | | |
|---|---|---|---|
| Injector: | 250 °C | | |
| Initial Temperature: | 40 °C | Final Temperature: | 280 °C |
| Initial Time: | 4 minutes | Final Time: | 2 minutes |
| Rate (°C/min): | 10 | Run Time: | 30 minutes |
| Flow: | 0.8 mL/minute (constant flow), Helium | | |
| Split Ratio: | 200:1 | | |

Gas Chromatograph Capillary Column (HP-1ms®)

| | |
|---|---|
| Column Phase: | 100% Dimethylpolysiloxane |
| Inside Diameter: | 250 µm |
| Film Thickness: | 0.25 µm |
| Length: | ≈ 30 meters |

Automatic Injector (Agilent® 7693)

Injection Volume: 1 µL

Mass Spectrometer (Agilent® 5975C)

| | |
|---|---|
| Acquisition Mode: | Scan, Electron Ionization (EI), Positive-Ion mode |
| Scan: | **15** to **120** m/z (1.3 to 2.05 minutes) |
| Scan: | **33** to **350** m/z (2.45 to 30.0 minutes) |
| Source: | 230 °C |
| Quadrupole: | 150 °C |

### Sample Preparation and Equipment

Gas Chromatograph/Mass Spectrometer (GC/MS) "Delta", Autotuned: **September 1, 2014**

Passive Headspace Extraction technique utilized a ≈ 40 $mm^2$ C-strip at **65 °C** for ≈ 18 hours, and eluted with ≈ 250 µL of Carbon Disulfide ($CS_2$) solvent

An empty metal paint can (AMPAC Fire Debris Bag®) contained a ≈ 40 $mm^2$ C-strip hanging on a Paper Clip and suspended by a String, and $CS_2$ Solvent Blanks were analyzed using identical conditions as all items

Activated Charcoal Strips® (C-strips), (Albrayco Technologies®) ACS-100, **Lot # D121312**

$CS_2$ solvent, HPLC grade (Aldrich Chemical Co.®), **Lot # 01928AJ**

Helium, chromatography grade (99.999+%)

C-strip portions returned as **Item # 100GW**

All items were analyzed by GC/MS and Wiley 9th / NIST 2011 MS Library® software

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# Appendix B

## Table 3

## Sequence Table Setup

1. Use the GC/MS computer
2. "Sequence"
3. "Edit Sequence" and enter the appropriate information
   - "Type" – sample
   - "Vial" – position number in autosampler tray
   - "Sample" – (blank) for laboratory #, evidence #
   - "Method" – GC/MS method (usually ARSON)
   - "Data File" – (blank) laboratory #, evidence #
   - "Comments" – initials, extraction solvent, dilution ratio
4. Repeat this process until the table is filled in
5. "OK"
6. "Save Sequence As …", (File name), (ex. 073114initials), "Save"
7. "Simulate Sequence" (to verify operability of sequence)
8. Modify the "Data File Directory" (ex. D:\Data\073114initials, "Run Sequence" **NOTE**: if an error occurs, modify the sequence
9. "Sequence", Print Sequence …, "Brief Format" (optional)
10. Review the Sequence Report to ensure that all the information is correct.
11. Ensure that the "rinse bottle" in the autosampler is full with the "Extraction Solvent"
12. Ensure that the syringe moves freely
13. "Sequence", "Run"
14. **Wait** until the first vial completes the injection

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## Table 4

### Extracted Ion Profiles

Macro Command

{C:\mschem\MSexe\deltaAKARION.MAC}

**macro "deltaakarion",go**

*(A copy of this macro is stored in the Fire Debris Instrument Logbook)*

## Table 5

### Extracted Ions for EIP Analysis

| Chemical Family | Extracted Ions (m/z) |
|---|---|
| Alkanes | 57, 71, 85, 99 |
| Cycloparaffins | 55, 69, 83 |
| Aromatics | 91, 105, 119 |
| Naphthalenes | 128, 142, 156 |
| Indanes | 117, 131 |

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# Appendix B

## Table 6

| Additional Chemical Families & Extracted Ions | |
|---|---|
| Compound Type | m/z |
| Alkane | 43, 57, 71, 85, 99 |
| Cycloalkane and alkene | 55, 69 |
| n-Alkylcyclohexanes | 82, 83 |
| Aromatic-alkylbenzenes | 91, 105, 119, 92, 106, 120,134 |
| Indanes | 117, 118, 131, 132 |
| Alkylnaphthalenes | 128, 142, 156, 170 |
| Alkylstyrenes | 104, 117, 118, 132, 146 |
| Alkylanthracenes | 178, 192, 206 |
| Alkylbiphenyls/acenaphthenes | 154, 168, 182, 196 |
| Monoterpenes | 93, 136 |
| Ketones | 43, 58, 72, 86 |
| Alcohols | 31, 45 |

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Appendix B **- Table 7**

**Ignitable Liquid Classification Scheme**

| Class | Light($C_4$-$C_9$) | Medium ($C_8$-$C_{13}$) | Heavy ($C_9$- $C_{20+}$) |
|---|---|---|---|
| Gasoline-all brands, Gasohol, E85 | Fresh gasoline is typically in the range $C_4$-$C_{12}$ | | |
| Petroleum Distillates (including De-Aromatized) | Petroleum Ether<br>Some Cigarette Lighter Fluids Some Camping Fuels | Some Charcoal Starters<br>Some Paint Thinners<br>Some Dry Cleaning Solvents | Kerosene<br>Diesel Fuel<br>Some Jet Fuels<br>Some Charcoal Starters |
| Isoparaffinic Products | Aviation Gas<br>Some Specialty Solvents | Some Charcoal Starters<br>Some Paint Thinners<br>Some Copier Toners | Some Commercial Specialty Solvents |
| Aromatic Products | Some Paint and Varnish Removers<br>Some Automotive Parts Cleaners<br>Xylenes, Toluene-based products | Some Automotive Parts Cleaners Specialty Cleaning Solvents<br>Some Insecticide Vehicles<br>Fuel Additives | Some Insecticide Vehicles<br>Industrial Cleaning Solvents |
| Naphthenic-Paraffinic Products | Cyclohexane based solvents/products | Some Charcoal Starters<br>Some Insecticide Vehicles<br>Some Lamp Oils | Some Insecticide Vehicles<br>Some Lamp Oils<br>Industrial Solvents |
| Normal-Alkanes Products | Solvents<br>Pentane<br>Hexane<br>Heptane | Some Candle Oils<br>Some Copier Toners | Some Candle Oils<br>Carbonless Forms<br>Some Copier Toners |
| Oxygenated Solvents | Alcohols<br>Ketones<br>Some Lacquer Thinners<br>Fuel Additives<br>Surface Preparation Solvents | Some Lacquer Thinners<br>Some Industrial Solvents<br>Metal Cleaners/Gloss Removers | |
| Miscellaneous/Other | Single Compound Products<br>Some Blended Products<br>Some Enamel Reducers | Turpentine Products<br>Some Blended Products<br>Some Specialty Products | Some Blended Products<br>Some Specialty Products |

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## Appendix C

## **Revision History**

This manual has too many revisions from FD 2013 R0 to document in a revision history. It must be read as a complete new document.

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