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OVERVIEW

Summary of Test Methods

The following protocols for extractions and interpretation of flammable liquid evidence in the Alaska Department of Public Safety Crime Detection Laboratory use the following ASTM standards as reference guides:

- E 1386 Standard Practice for Separation and Concentration of Ignitable Liquid Residue from Fire Debris Samples by Solvent Extraction
- E 1388 Standard Practice for Sampling of Headspace Vapors from Fire Debris Samples
- E 1412 Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris by Passive Headspace Concentration
- E1618 Standard Test Methods for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry
- E 1387 Ignitable Liquid Classification System

The method 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 current chromatograms (TICs) are evaluated by visual pattern matching against known standards for the purpose of detecting and identifying ignitable liquid residues. Specific ions are indicators of certain classes of compounds, so extracted ion profiles from ASTM E1618 are included for guidance in standard to sample comparisons.

Significance and Use

The identification of ignitable liquid residues in samples from a fire scene may assist the fire investigator regarding the origin, fuel load, cause, and incendiary nature of the fire.

The identification of ignitable liquid residue 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 liquid residues.

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

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Materials normally found in buildings, upon exposure to the heat of a fire, will form pyrolysis and combustion products. Extracted ion profiling may facilitate the identification of an ignitable liquid in the extract by reducing interference by components generated as products of pyrolysis.

EVIDENCE COLLECTION

Fire Debris evidence should be collected and sent to the laboratory in quart or gallon paint cans or fire debris bags. It is important to collect the evidence as soon as possible and place into an air tight container. Use new and clean lined metal paint cans (the interior has a coating, usually grey) or heat sealed plastic bags approved for fire debris. Collection containers are regularly checked with new lot numbers to assure that no contamination is present to interfere with the analysis. Paper bags, non-fire debris plastic bags, or glass bottles should NOT be used.

Fill no more than $\frac{3}{4}$ or less of the capacity of the container to leave room for air space. Use optimal size cans that match the amount of evidence.

If liquids are to be sent to the laboratory as evidence, a new leak-proof glass vial, tightly sealed with a Teflon cap, that contains approximately 2 mL (approximately 20 drops) of liquid is the preferred method. Only a representative sample should be sent in to the laboratory. If a container needs to be fingerprinted, it should be submitted as a separate item with any liquid removed.

Disposable gloves should be changed between the collection of each sample. These gloves should not be submitted.

Any tools used in the collection of evidence should be cleaned between samples.

Collect a comparison sample (control sample) of similar debris away from the target area collected. For example: a portion of carpet in the corner of room which is not suspected of having an accelerant.

INSTRUMENTATION, EQUIPMENT, & MATERIALS

1. Gas Chromatograph/Mass Spectrometer (GC/MS)
-system designated as "Moe"

This laboratory utilizes:

- Agilent Gas Chromatograph with an autosampler
 - Mass spectrometer (MSD)
 - Approximately 30 meter x 0.25 mm HP-1ms (DB-1, etc.) fused silica capillary column coated with 100% methyl silicone film thickness of 0.25 μ m is used. A phenylmethyl silicone column such as a HP-5ms (DB-5, etc.) may also be used.
 - Mass spectrometer capable of scanning from 30-400 m/e.
 - Computer and software with ability to control GC and MS, retrieve mass spectral data, and compare to a library
 - Carrier gas: chromatography grade helium (obtained from Air Liquide™)
2. Reference ignitable liquid collection
 3. Oven, forced air, with temperature control from ambient to 150°
 4. Reagent grade (or better) carbon disulfide and pentane
 5. Charcoal adsorption strips-polymer strips used to adsorb organic vapors (available from Albrayco Laboratories)
 6. Other consumables: paint cans, fire debris bags, vials, inserts, caps, pipets, paper clips, magnets, razor blades, thread, gas-tight syringes

QUALITY CONTROL

1. Calibration

The MS is tuned at least once per month that the instrument is in use. Records are maintained in the LIMS: CS INST 2012 (or current year).

2. Standard

Standard Accelerant Mixture is run with every case (or batch of cases).

Standard Accelerant Mixture (A.M.)

Stock: equal parts gasoline, kerosene, and diesel fuel
Working: Stock mixture diluted to approximately 5% with carbon disulfide (C₂S)

3. Test Mixtures

These are analyzed several times a year to test the sensitivity and resolution of the component peaks. Results are recorded in LIMS.

Cerilliant Resolution Test Mixture (catalog number ERR-002)

Restek E-1618-97 Test Mixture (catalog number 31613)

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4. A **blank sample** is generated whenever new evidence from a case is analyzed, utilizing a new activated charcoal strip (c-strip), new vial, new insert, and carbon disulfide. A previous 'blank' paint can, a new paint can, or a new fire debris bag is used for the extraction. This blank sample is analyzed prior to all samples from casework.

Instrument Quality Control documentation is maintained and archived in the GC/MS Logbook for the instrument (designated as Moe) and/or the laboratory's LIMS.

Chemical and Equipment Quality Control is maintained in the Fire Debris Quality Control Logbook and/or the laboratory's LIMS.

The gas chromatograph and mass spectrometer are cleaned and maintained as needed (source, septa, liner etc.). See instrument logbook.

Instrument syringes are rinsed thoroughly between sample injections.

Blank sample analyses are documented in the individual case files.

Every case file includes a standard TIC chromatogram, either the working Accelerant Mixture or an appropriate standard from the reference ignitable liquid collection. The standard chromatograms are analyzed under the same chromatographic and mass spectral conditions as those used to produce the evidence TIC chromatogram.

At least one standard and a blank are included in every sequence of samples on the GC/MS.

Activated charcoal strips (c-strips), carbon disulfide, fire debris bags, pentane, razor blades, paper clips, magnets etc. are purchased and stored to ensure they are free of extractable hydrocarbons. Additionally, new lot numbers of carbon strips, fire debris bags, and carbon disulfide are analyzed before use to insure that no contamination is present.

1. One representative adsorbent charcoal strip from each new lot should be analyzed in the same manner as an actual case to insure the quality of the products adsorption efficiency and the lack of contaminants. Documentation will be maintained in the Fire Debris Quality Control Logbook.

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2. The adsorption efficiency of the activated carbon strip is periodically checked by running the passive headspace extraction procedure on a known volume of Accelerant Mixture (AM).
3. The solvent purity is checked by evaporating the carbon disulfide to at least half the original volume. The evaporated solvent is analyzed by GC/MS and documented in the Fire Debris Quality Control Logbook.

A negative carbon strip and solvent extraction control is included with each batch of samples to show that no cross-contamination has occurred. This solvent blank is analyzed before each evidence sample and documentation is found in the case file. Significant amounts of contaminants in the blank control need to be investigated and documented prior to the issuance of a report. Repeating the negative control may be necessary. Results will not be reported until any contamination issues have been resolved.

The temperature of the oven used should be 65°C plus or minus 15°. The temperature is monitored before samples are placed in the oven *and* when the samples are removed. Records are maintained for the periods that the oven is used.

Certified ignitable liquid standards are not necessary. Most reference ignitable liquids can be obtained from commercial and retail sources.

SEPARATION and CONCENTRATION PROCEDURES

Passive Headspace Concentration

This procedure is used for sampling ignitable liquid residue from samples of fire debris. The method is nondestructive. It is the method of choice for fire debris evidence that is packaged in airtight containers (i.e. paint cans or fire debris bags). Passive Headspace Concentration may not distinguish between #1 and #2 fuel oils, waxes, vegetable oils, engine oils, bunker oils, lubricating oils, etc. It also may not detect light oxygenated solvents and 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 an adsorbent charcoal strip (typically a full size strip) on the end of a new and clean 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 thread.
- 3) Reseal the container and place in an oven set to approximately 65° C overnight. Extraction temperature and time can vary from 50° to 80° C and 2 to 24 hours. Longer times or higher temperatures are required for the adsorption of higher boiling point compounds, dense sample matrices, or for adsorption of very small quantities of volatile hydrocarbons. The adsorption temperature and duration may vary based on the sample. CAUTIONARY NOTE: When other evidentiary considerations arise, such as document or latent print examinations, it may be appropriate to conduct the adsorption at ambient temperature (approximately 20° to 25° C) for extended periods (24 hours or longer) to minimize damage. Room temperature adsorption may also be appropriate to detect low molecular weight compounds.
 - 4) After heating, the container is removed from the oven and is allowed to cool to room temperature.
 - 5) The charcoal strip is removed from the container and divided into two pieces. One portion is placed in an appropriately labeled vial and returned with the evidence. The other is placed into a labeled auto sampler vial with insert. Carbon disulfide is added to the vial insert and the vial sealed with a screw cap septum. The sample is now ready for instrumental analysis.
 - 6) A parameter sheet containing the lot number and amount of the adsorbent, the approximate oven temperature, the approximate length of time in the oven, the elution solvent type, and approximate elution volume is included with the case file. Information is also included regarding the column and the GC/MS parameters.

Solvent Extraction of fire debris or containers

Due to size and/or packaging, certain items may not be suited for using the passive adsorption 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.

- 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 pentane or carbon disulfide.
- 4) For some items of evidence (such as fuel cans) the solvent may be added directly to rinse any ignitable liquid residues.
- 5) Decant the solvent into a second clean beaker and filter if necessary.
- 6) Reduce the eluent volume in a hood by allowing it to evaporate to approximately 1 mL to concentrate any ignitable liquid residues that may be present.
- 7) The sample is now ready to be transferred to an autosampler vial for instrumental analysis. The elution extract is returned with the evidence after it is analyzed by GC/MS.

Sampling of Head Space Vapors from Fire Debris Samples

This method may be employed when the investigator suspects that a light oxygenate may be present, an odor of alcohol is detected, and 'negative' results are obtained using the passive headspace method.

This practice is the least sensitive of the sample preparation techniques and may not detect quantities of less than 10 μ L 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 chromatograms 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 sample in order to determine that it is consistent with its description. Resolve any discrepancies.
- 2) A gas-tight syringe blank consisting of air is analyzed on the GC/MS using an appropriate method.
- 3) Punch a small hole in the lid of the paint can with a tool such as an awl and immediately place a piece of transparent tape over the hole.
- 4) Try a room temperature sampling first, then place the can in an oven at approximately 65°C for about 30 minutes.
- 5) Insert the syringe needle through the taped hole, pump it several times, and withdraw approximately one milliliter of headspace sample. Inject into the GC/MS using an appropriate temperature program.
- 6) Reseal the hole with tape.

Liquid Samples

If a liquid sample is submitted, a flame test may be run. This may be accomplished by placing a few drops of the liquid into a non-flammable container such as metal weighing boat and then exposing the liquid to a flame. The results of this test are then documented in the bench notes. The pH of the liquid may also be determined.

Clean liquid samples may be injected into the GC/MS after dilution of the sample with carbon disulfide at an approximate ratio of 1:100.

INSTRUMENTAL ANALYSIS (Gas Chromatography/Mass Spectrometry)

Utilizing one of the above described extraction techniques, a sample is obtained for analysis by GC/MS. The resulting total ion chromatogram, mass spectral data, and extracted ion profiles are then evaluated by comparison to known standard data.

GC parameters

Injector	250° C
Initial Temperature:	40°
Initial Time	4 minutes
Rate	10°/minute
Final Temperature	280°
Final time	2 minutes
Total run time	30 minutes

MS parameters

Inlet	GC
Acquisition mode	Scan
Low mass	31
High mass	350

Note: These are suggested conditions only. Other parameters may be used as long as suitable resolution is obtained. HOWEVER, the preferred policy is for all fire debris chemists to agree on standard instrumental conditions so that all can become acquainted with the patterns generated. Any changes to the instrumental SOP must be authorized and distributed by the supervisor of the discipline. Questioned samples and known standards must be run using the same conditions.

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Analysis setup:

1. On the data station computer, select MSD icon.
2. From the menu bar select SEQUENCE.
3. Choose EDIT SAMPLE LOG TABLE and enter the appropriate information:
 - TYPE – sample, blank, or calibration standard
 - VIAL – position number in autosampler tray
 - METHOD – desired parameters (usually EMARSON1)
 - SAMPLE NAME – laboratory number and item number, blank or sample

Repeat this process until all data is entered. Select OK and review the sequence table to ensure that all vials are logged correctly. Check the level of solvent in rinse vials on the autosampler, select SEQUENCE, then RUN.

DATA

1. Access to data:
 - On the data station computer, select ENHANCED DATA ANALYSIS icon
 - From the menu bar select FILE
 - Choose LOAD DATA FILE and select desired data file
 - To display the mass spectrum of a peak on the chromatogram, double right click on the peak.
 - To show library matches, double right click on the mass spectrum.
 - Total ion chromatograms with mass spectral data as well as extracted ion profiles from evidence samples and standards are utilized in reporting decisions and are retained in the LIMS case file.
 - Raw data files are retained for technical review use.
2. Initial data analysis consists of a visual comparison of the total ion chromatogram to reference ignitable liquid chromatograms. The essential requirement for making a classification is noting points of correlation and similarities between the sample chromatogram and the reference ignitable liquid chromatogram obtained under the same conditions. Pattern matching requires that the entire pattern used for comparison be displayed at a comparable sensitivity. External libraries are intended only to give guidance for selection of reference ignitable liquids. The mass

spectrum of major peaks may be compared to the NIST98 or another suitable library.

3. The carbon number range is determined by comparing the chromatogram to a reference or test mixture containing known normal alkanes.
4. Mass chromatography may be carried out using selected ion analysis.

Chromatograms

The GC/MS data station computer is used to display total ion chromatograms as well as extracted ion profiles for various types of compounds. Individual extracted ion profiles for two or more characteristic ions of the same functional groups or of similar magnitude may be summed to enhance the signal-to-noise ratio and to decrease interference by extraneous compounds that contain only one of the ions or to create summed profiles characteristic of specific classes of hydrocarbons.

Total ion current chromatograms for an unknown sample are compared against the corresponding TICs from reference material samples. This is generally done by visual pattern recognition.

Major peaks in the TIC should be identified by searching their mass spectra against a suitable library. The final identification must be made on the basis of the mass spectra and retention times of the compounds in question by comparison to reference materials.

INTERPRETATION

Ignitable liquids usually consist of compounds in different chemical families, and have been organized into the following classification system, based on ASTM E1618 (Table 1):

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Table 1

Class Name	Peak Spread	Examples
Light Petroleum Distillate	C4 - C9	Petroleum ethers, pocket lighter fuels, some rubber cement solvents, Skelly solvents, V M & P Naphtha, some camping fuels
Gasoline	C4 - C12	All brands & grades of automotive gasoline, including gasohol
Medium petroleum Distillate	C8 - C13	Mineral spirits, some paint thinners, some charcoal starters, dry cleaning solvents, some torch fuels, some solvents for insecticides and polishes, some lamp oils
Heavy Petroleum Distillate	C9 - C20+	No. 1 & No. 2 fuel oil, kerosene, diesel fuel, some jet fuels, some charcoal starters, some solvents for insecticides
Miscellaneous	Variable	Single compounds, turpentines, enamel reducers, specialty mixtures that cannot be further classified into one of the categories below.
Oxygenated Solvents	Variable	Alcohols, esters, ketones
Isoparaffinic Products	Variable	Some charcoal starters, some copier toners, some aviation gasolines, some lamp oils, some specialty/industrial solvents
Normal Alkanes	Variable	Specialty products formulated from normal alkanes, some lamp oils, copier toner, carbonless paper
Aromatic Products	Variable	Specialty cleaning solvents, fuel additives, some paint and varnish removers, some automotive parts cleaners, xylenes, toluene based products
Naphthenic Paraffinic Products	Variable	Some charcoal starters, some paint thinners, some insecticide vehicles, some lamp oils, industrial solvents

The significant compounds that comprise ignitable liquids consist of six major types:

- Alkane (both normal and branched)
- Alkene
- Cycloparaffin
- Aromatic
- Polynuclear aromatic
- Oxygenates

Other compounds may be present, but are not considered significant for the purposes of this method.

Under the ignitable liquids classification system presented in Table 1, eight major classes of ignitable liquids, plus gasoline, may be identified by gas chromatography/mass spectrometry and ion profiling when recovered from fire debris. This is because the distillates are divided into light, medium, and heavy categories and a miscellaneous category is included for those ignitable liquids that do not fall into one of the major ignitable liquid classifications.

This method is intended to allow identified ignitable liquids to be characterized. Distinguishing between examples within a class may be possible, but not consistent.

The products listed in Table 1 in the various classes are illustrations of known commercial uses these ignitable liquids have. These examples are not intended to be all-inclusive.

Some products are found in multiple classifications, such as "charcoal starters." Therefore, many of the examples can be prefaced by the word "some," as in "some charcoal starters."

Compounds of each type produce characteristic major ion fragments. These ions are listed in Table 2:

TABLE 2 Major Ions Present in Mass Spectra of Common Flammable and Combustible Liquids

Compound Type	m/e
Alkane	43, 57, 71, 85, 99
Cycloalkane and alkene	55, 69
<u>n</u> -Alkylcyclohexanes	82, 83
Aromatic-alkylbenzenes	91, 105, 119; 92, 106, 120
Indanes	117, 118; 131, 132
Alkyl-naphthalenes	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
R. Martin Smith, <u>Analytical Chemistry</u> , Vol. 54, No. 13, November 1982, pp. 1399A-1409A.	

1. With the exception of the gasoline class, the major ignitable liquid classes may be divided into 3 subclasses based on boiling range: Light, Medium and Heavy.
2. Light product range: C₄-C₉, the majority of the pattern occurs in the range C₄-C₉, no major peaks exist above C₁₁.
3. Medium product range: C₈-C₁₂, narrow range products, the majority of the pattern occurs in the range C₈-C₁₂, no major peaks below C₇ or above C₁₄.
4. Heavy product range: C₉-C₂₃, typically broad range products, the majority of the pattern occurs in the range C₉-C₂₃, with a continuous pattern spanning at least 5 consecutive normal hydrocarbons, or ignitable liquid products starting above C₁₁.
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.
6. In order for an extract to be characterized as containing a particular class, the following minimum criteria must be met:

Criteria for the Identification of Gasoline

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

ALKANE: Petroleum distillate pattern comparable to that of a known standard with alkanes above C₉ present.

CYCLOALKANES: Not present in significant amounts.

AROMATIC: Petroleum distillate pattern comparable to that of known standards; 1-methyl-3-ethylbenzene (*n*-ethyltoluene), 1-methyl-4-ethylbenzene (*p*-ethyltoluene), 1, 3, 5-trimethylbenzene, 1-methyl-2-ethylbenzene (*o*-ethyltoluene), and 1, 2, 4-trimethylbenzene (pseudocumene) *must be present*; above C₇, the aromatic concentration is generally substantially higher than the alkane concentration.

CONDENSED RING AROMATIC: Pattern comparable to known standard 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.

CAUTIONS: 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.

Criteria for the Identification of Distillates

GENERAL: Traditional distillates and de-aromatized distillates; pattern typified by a Gaussian distribution of peaks with or without aromatic product present.

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

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

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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 Identification 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 component pattern are dependent on the specific formulation.

AROMATIC: Not present at significant concentrations.

CYCLOALKANES: Not present at significant concentrations. Note: Ions indicative of cycloparaffins are also present in smaller amounts in isoparaffinic compounds. "Cycloalkane" pattern representing isoalkanes may be present, but significantly less abundant than the alkane pattern.

CONDENSED RING AROMATICS: Not present.

Criteria for the Identification of Aromatic Products

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

ALKANE: Not present in significant amounts.

CYCLOALKANES: Not present in significant amounts.

AROMATIC: 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 few components. These compounds must be identified by both GC retention time and mass spectral identification.

Criteria for the Identification 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. Examples are low-odor solvents and paint thinners.

ALKANES: Abundant. Normal alkanes may be notably absent or diminished. Depending on the feed stock (both de-aromatized distillates and de-aromatized, de-paraffinated distillates may be used), normal alkanes may be present, but at diminished levels compared to distillate products. Pattern comparable to known naphthenic paraffinic products.

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

AROMATICS: Not present in significant amounts.

CONDENSED RING AROMATICS: Not present in significant amounts.

Criteria for the Identification of Normal Alkane Products

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

ALKANE: Normal 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 significant.

AROMATIC: Not significant.

CONDENSED RING AROMATIC: Not significant.

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

Criteria for the Identification of Oxygenated Solvents

GENERAL: Products containing major oxygenated components may include mixtures of oxygenated compounds and other compounds or products. Major oxygenated compounds present before C8; major compound(s) may include alcohols, esters, 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.

AROMATIC: Pattern depends on formulation.

CONDENSED RING AROMATIC: Not significant.

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

CAUTION: 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 other peaks in the chromatogram) before the analyst should consider the finding of an oxygenated product significant.

Miscellaneous (Others)

No classification system is likely to describe all possible ignitable liquids. Flammable non-petroleum-based products, such as turpentine, do not fall into any of the categories. The Miscellaneous category exists for these products.

Identification of an ignitable liquid must be based on retention and mass spectra characteristics.

Factors Affecting Interpretation of Results

Pattern matching of total ion current chromatograms or extracted ion profiles rarely gives perfect correlation with reference material. 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 either the light end or the heavy end of the chromatogram or ion profiles, or both. Under certain conditions, selective loss of classes of compounds may result from microbiological degradation. Compounds may also be added to the pattern when the pyrolysis of materials at the fire scene yields compounds of the same type as those being compared. All of these circumstances must be taken into account by the analyst during visual pattern evaluation. It is therefore imperative that the analyst have a sufficient library of commercially available 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 Components-Burned material from which the sample has been extracted usually contributes extraneous components 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 paraffinic,

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cycloparaffinic, aromatic, or condensed ring aromatic hydrocarbons, all of which will appear in the total ion chromatograms.

Extracts that meet the criteria for heavy petroleum distillates should be reviewed carefully for "extraneous components" 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 1/2 an order of magnitude) of the alkane, should be considered as indicating the presence of polyolefin products rather than fuel oil products. Polyolefin decomposition products typically do not exhibit the same pattern of branched alkanes as fuel oils.

Missing Components-Exposure of the ignitable liquid to heat usually results in the preferential loss of lighter components, thereby enhancing the chromatographic pattern at the heavy end. Some sample preparation techniques may result in the preferential recovery of either the lighter or heavier components, resulting in the "loss" in the opposite end. Neither of these factors will cause the selective loss of intermediate components. The unexplainable absence of components 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 aromatic-containing polymers may include toluene and xylenes. The pyrolyzates of asphalt and polyolefin plastic may include a homologous series of normal alkanes.

Certain ignitable liquid components may be found in some substrates at the fire scene. Examples include:

- normal alkane products found in linoleum and in carbonless paper forms
- distillates found in some printed materials
- certain 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 or not an ignitable liquid is foreign to the substrate.

Factors Affecting Interpretation

1. Some samples are weathered (partially evaporated) when received
2. Distortion of the total ion chromatogram because of components being trapped in the matrix more firmly than others
3. Components being lost because of bacterial action
4. Contamination due to either low concentrations of sample or high concentration of interfering components
5. Mixtures of ignitable liquids
6. The complete spectrum of one substance overlaps another
7. Weathered samples of one sample resembling weathered samples of another

CASE FILE

The bench notes will contain:

- Fire Debris Worksheet
- The analyst's name (or initials) and laboratory case number on each page of file
- A description of each item of evidence and its packaging
- A description of the instrument and column parameters
- Documentation of instrument tune within one month
- Extraction method used (e.g. passive headspace) for each item
- Extraction details such as oven temperature and adsorption time.
- Lot number of activated charcoal strips (when used)
- Standard Accelerant Mixture Total Ion Chromatogram
- Blank TIC from activated charcoal strip (with passive headspace), elution solvent, and/or empty fire debris container.

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- Mass chromatograms of all evidence items
- Extracted ion profiles when utilized for interpretation
- Blank TIC for each evidence item analyzed by GC/MS
- Total and extracted ion profiles for standards utilized for comparison
- Conclusions reached from analysis
- Disposition of adsorbed but unused charcoal strips
- Dates that analysis began and was completed.

The LIMS case file will also contain:

- 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

The REPORT will contain:

- Agency case number
- Submitting Agency
- Name of person submitting evidence
- Item numbers and descriptions of submitted evidence
- Results of laboratory analysis

The report may contain examples of commercial products and/or substrates that might contain the ignitable liquid identified. The conclusion should give the analyst's opinion as to whether or not an ignitable liquid was identified in the sample. If a negative result was obtained, a disclaimer may be offered to the effect that it does not preclude the possibility that ignitable liquids were present at the fire scene. In the case of a positive report, it may be appropriate to add a disclaimer to the effect that the identification of an ignitable liquid residue in a fire scene does not necessarily lead to the conclusion that a fire was incendiary in nature. Terms such as hydrocarbons, consistent with, in the boiling range of, similar to, or characteristic of will not be used without additional explanation or a positive identification of the product. Results may be reported using the classification presented in Table I or as a light, medium, or heavy petroleum product. See the explanation following Table I for further guidance. Ignitable liquids may be classified by the guidelines appearing in ASTM E1618.

REFERENCES

GC-MS Guide to Ignitable Liquids, Reta Newman, CRC Press, 1998.

ASTM Standard E 1386-00: Standard Practice for Separation and Concentration of Ignitable Liquid Residue from Fire Debris Samples by Solvent Extraction.

ASTM Standard E 1387-01: Standard Test Method for Ignitable Liquid Residues in Fire Debris Samples by Gas Chromatography.

ASTM Standard E 1388-00: Standard Practice for Sampling of Headspace Vapors from Fire Debris Samples.

ASTM Standard E 1412-00: Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration.

ASTM Standard E 1618-10: Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography/Mass Spectrometry.

R. Martin Smith, Analytical Chemistry, Volume 54, Number 13, November 1982.

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APPENDIX A Abbreviations

~: approximately

AM or SAM: Accelerant Mixture or Standard Accelerant Mixture

ASTM: American Society for Testing and Materials

c-strip: activated charcoal strip

GC: gas chromatograph

EIC: extracted ion chromatogram (mass chromatogram)

EIP: extracted ion profile

LIMS: Laboratory Information Management System

m/z: mass to charge ratio

µL: microliter

MS: mass spectrometer

PHS: passive headspace

TIC: total ion current chromatogram

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APPENDIX B Review Checklist

TECHNICAL REVIEW

Analyst:

Date:

Yes N/A

- | | | |
|--------------------------|--------------------------|--|
| <input type="checkbox"/> | <input type="checkbox"/> | The container and a brief description of its contents are documented. |
| <input type="checkbox"/> | <input type="checkbox"/> | The sample preparation and analytical technique performed is recorded. |
| <input type="checkbox"/> | <input type="checkbox"/> | The GC conditions are documented. |
| <input type="checkbox"/> | <input type="checkbox"/> | The GC/MS tune has been done as needed or within approximately one month. |
| <input type="checkbox"/> | <input type="checkbox"/> | The carbon strip lot #, oven temperature, and the adsorption time are recorded. |
| <input type="checkbox"/> | <input type="checkbox"/> | The Standard Accelerant Mixture and solvent blank from the time period of the analysis are included. |
| <input type="checkbox"/> | <input type="checkbox"/> | For each GC/MS data file, a blank is included in the notes. |
| <input type="checkbox"/> | <input type="checkbox"/> | For each identified ignitable liquid, a standard (or use of the AM) is included.. |
| <input type="checkbox"/> | <input type="checkbox"/> | Bench notes include an explanation of identifying characteristics (if applicable). |
| <input type="checkbox"/> | <input type="checkbox"/> | The analyst's conclusions in the report are supported by documentation in the Case file. |
| <input type="checkbox"/> | <input type="checkbox"/> | The disposition of the unused carbon strip portion is documented. |
| <input type="checkbox"/> | <input type="checkbox"/> | The worksheet indicates the dates that analysis was started and completed. |
| <input type="checkbox"/> | <input type="checkbox"/> | All of the bench notes, instrumental data and worksheet are in LIMS. |

ADMINISTRATIVE REVIEW

Analyst:

Date:

Yes N/A

- | | | |
|--------------------------|--------------------------|---|
| <input type="checkbox"/> | <input type="checkbox"/> | The requesting agency, agency number, & laboratory number agree between the laboratory request and the laboratory report. |
| <input type="checkbox"/> | <input type="checkbox"/> | The correct submitting officer or whom to reply to appears on the report. |
| <input type="checkbox"/> | <input type="checkbox"/> | Item numbers & descriptions agree between LIMS, bench notes, spectra & report. |
| <input type="checkbox"/> | <input type="checkbox"/> | Grammar and punctuation are correct. |
| <input type="checkbox"/> | <input type="checkbox"/> | The report is signed by the analyst. |
| <input type="checkbox"/> | <input type="checkbox"/> | All of the bench notes and attached/scanned documents are present in LIMS. |
| <input type="checkbox"/> | <input type="checkbox"/> | The report is referred for release to the submitting agency. |
| <input type="checkbox"/> | <input type="checkbox"/> | The electronic chain-of-custody in LIMS agrees with the worksheet and report. |

APPENDIX C ASTM Documents

See the laboratory network:

I:\Discipline Shares\Fire Debris\ASTM Documents

APPENDIX D Uncertainty of Measurement

Since fire debris analysis is a qualitative testing method, the term *measurement* does not apply.

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Appendix E Revision History

Section(s) Revised	Date	Issuing Authority
Header , added "Analysis" to manual title.	1-14-2012	Jane Booth, Supervisor
Overview , p. 3, removed American Society for Testing Materials and year designations of publications. Changed "data system" to "data station (computer)". Removed Chemstation™. Removed redundancy in referring to extracted ion profiles. Corrected formatting error at <u>E 1618</u> . Changed "field" investigator to "fire" investigator. Page 4, removed "and target compound identification techniques described".	1-14-2012	Jane Booth, Supervisor
Evidence Collection , p. 4, added "new and clean" and "quart or gallon" to description of paint cans and removed brand names. Added "heat sealed" and "plastic" to description of fire debris bags and removed brand name. Added list of unsuitable containers or packaging. Revised protocols for submission of liquid samples. Added "disposable" to glove description.	1-14-2012	Jane Booth, Supervisor
Instrumentation, Equipment, & Materials , p. 5, changed H.P. to Agilent & removed model numbers. Changed "Chemstation™" to "computer" and added ability of computer software to control the GC and MS. Added supplier of helium. Added gas-tight syringes to list of consumables.	1-14-2012	Jane Booth, Supervisor
Quality Control , pp. 5-7, changed LIMS electronic file to 2012. "SAM" changed to "Accelerant Mixture", working concentration changed to <i>approximately</i>	1-14-2012	Jane Booth, Supervisor

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<p>5%. Changed “run” to “analyzed”, changed test mixture information from “catalogue” to “catalog”. Removed “Justice Trax”. MS and GC cleaned and maintained “as needed”. Changed syringes “cleaned” to syringes “rinsed”. Added “TIC” to standard chromatogram. Changed “tested” to “analyzed”. Changed Quality “Assurance” to Quality “Control”. Added further description of negative, blank, or solvent control. Explained monitoring of oven temperature.</p>		
<p>Separation and Concentration Procedures, pp. 7-8, changed “arson” samples to “fire debris” samples. Removed “jars” and expanded on the limitations of passive headspace analysis. Added “new and clean” to paper clip. Added “CAUTIONARY NOTE:” to precautions when other examinations are requested. Added “to room temperature” after “allowed to cool”.</p> <p>p. 9, changed “Evaporate the eluent to a small volume” to “Reduce the volume of the eluent in a hood by allowing it to evaporate”. Changed “placed” to “transferred to”.</p> <p>p. 9, removed “This method is not routinely utilized,” changed “involved” to “may be present”, added odor “of” alcohol, and removed “ester” and “ketone”. Changed “variables” to “inconsistencies”, removed “prior to headspace sampling”, & changed “components” to “compounds”. Changed “run” to “analyzed”, “sample” can to “paint” can, added “transparent” to tape. Added “Try a room temperature sampling first, then” place the can...Remove “The optimum sample size will vary with</p>	<p>1-14-2012</p>	<p>Jane Booth, Supervisor</p>

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<p>sample concentration.”</p> <p>p. 10, moved flame test paragraph to immediately after Liquid Samples and added optional determination of pH.</p>		
<p>Instrumental Analysis, p. 10, addition of pH measurement to liquid samples. Remove higher (>280°) temperature from GC parameters. Add that consensus on one single instrumental program will help prevent confusion with pattern recognition. Changed “lab” to “laboratory” throughout manual.</p>	1-14-2012	Jane Booth, Supervisor
<p>Data, pp. 11-12, change “mass chromatograms” to “chromatograms”. Change Chemstation™ to “data station computer” and changed purpose to display TICs and EIPs for various types of compounds. Removed paragraph “Target Compound Analysis”</p>	1-14-2012	Jane Booth, Supervisor
<p>Interpretation, pp. 12-19, re-worded first sentence and changed E1387 to E1618. Added “Table 1” to top of table. Explained 8 categories plus gasoline and <i>miscellaneous</i>. Changed “scheme” to “classification system”. Addressed identification of examples within a class. Added Table 2 citation to “References”, p. 25. Added examples of naphthenic paraffinic products. Changed “mass chromatograms” to “TIC chromatograms or extracted ion profiles”. Removed “target compounds”.</p>	1-16-2012	Jane Booth, Supervisor
<p>Interferences p. 20, Removed section of paragraph dealing with pyrolysis target compounds and Tables 3, 4, and 5. Under “Missing Components” deleted “compound did not meet target identification criteria”. Page 21, item 6, changed “substance being included in” to</p>	1-16-2012	Jane Booth, Supervisor

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"compound overlaps".		
Case File , pp. 21-22, removed 5% from Accelerant Mixture, changed "spectra" to "TIC", "Test spectra" to "Mass Chromatograms", and added information on page numbering in LIMS.	1-16-2012	Jane Booth, Supervisor
References , p. 23, removed 'year' designations from ASTM Standards.	1-16-2012	Jane Booth, Supervisor
Appendix A, Abbreviations , p. 24, added "Moe, LIMS, mass chromatogram, PHS, ~, c-strip, EIP, and AM or SAM". Removed "TCC". Altered definition of "ASTM and TIC". Changed "m/e" to "m/z".	1-16-2012	Jane Booth, Supervisor
Appendix B, Review Checklist , p. 25, changed "5% SAM" to "Accelerant Mixture", changed GC/MS "spectra" to "data file". Changed all references for "lab" to "laboratory".	1-16-2012	Jane Booth, Supervisor
Appendix C, ASTM Documents , p. 28, corrected network site for document storage after labwide data reorganization.	1-16-2012	Jane Booth, Supervisor

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