

Fire Debris and Ignitable Liquids Analysis

1 Scope

This procedure describes the general process for fire debris and ignitable liquids analysis. This procedure is suitable for most fire debris samples and can be used to identify single compounds, mixtures, and non-petroleum based ignitable liquids. Examples of sample matrices include debris from fire scenes, clothing, soil, or liquids.

This procedure applies to caseworking personnel that are qualified to examine evidence for the presence of ignitable liquids.

2 Equipment/Materials/Reagents

Equivalent equipment, materials, and reagents may be substituted as needed.

2.1 Equipment

- Fourier transform infrared spectrophotometer (FTIR)
- Gas chromatograph-mass spectrometer (GC/MS)
- Oven (capable of heating from 60°C to 90°C)

2.2 Materials

- Charcoal strips (e.g., Albrayco) cut into approximately 1 cm x 1 cm squares
- Cotton-tipped applicators
- Disposable 20 mL air-tight syringe and needle assembly
- Filter paper
- Nail
- New metal cans with friction fit lids (“paint cans”)
- Nylon bags
- Scissors
- Stainless steel or galvanized wire, small paper clips
- Tape
- Test tubes, beakers, pipettes, and autosampler vials

2.3 Reagents/Solvents/Reference Materials

- Acetone (reagent grade)
- Air (compressed)
- Carbon disulfide (reagent grade)

- Deionized water (18.2 megohm)
- Ethanol (reagent grade)
- Hexane (reagent grade)
- Ignitable liquids resolution test mixture (e.g., Restek E1618 Test Mix)
- Isopropyl alcohol (reagent grade)
- Methanol (HPLC grade)
- Methyl ethyl ketone (reagent grade)
- Nitrogen gas (high purity)
- Nitromethane (reagent grade)
- Pentane (reagent grade)
- Reference materials – A collection of commercially available fuels, solvents and specialty products such as gasoline, fuel oil #1, and fuel oil #2
- Toluene (reagent grade)

3 Standards and Controls

3.1 Headspace GC/MS Volatiles Test Mix

The volatiles test mix is a 0.01% (0.1 $\mu\text{L}/\text{mL}$) solution of methanol, ethanol, isopropyl alcohol, methyl ethyl ketone, nitromethane, acetone, and toluene in 18.2 megohm deionized water.

A 0.1% (1.0 $\mu\text{L}/\text{mL}$) intermediate stock solution is prepared by initially adding approximately 50 mL of deionized water to a 100-mL volumetric flask. Then, 100 μL of each individual pure component is pipetted into the volumetric flask and it is diluted to volume with deionized water. The 0.01% test mix solution is prepared by adding 10 mL of the intermediate stock solution to a 100-mL volumetric flask and diluting to volume with deionized water.

Alternatively, the 0.01% test mix may be directly prepared by initially adding approximately 50 mL of deionized water to a 100-mL volumetric flask. Then, 10 μL of each individual pure component is pipetted into the volumetric flask and it is diluted to volume with deionized water.

The test mix and intermediate stock solution will be maintained in glass bottles in a refrigerator.

3.2 Standard Accelerant Mix (SAM)

The SAM is a 0.05% (0.5 $\mu\text{L}/\text{mL}$) solution of gasoline, diesel, and kerosene (1:1:1) in carbon disulfide, hexane, or methanol.

A 0.5% (5.0 $\mu\text{L}/\text{mL}$) intermediate stock solution is prepared by adding 500 μL each of pure gasoline, diesel, and kerosene to a 100-mL volumetric flask and diluting to volume with carbon disulfide or another appropriate solvent.

The 0.05% standard is prepared by adding 5 mL of the 0.5% stock solution to a 50-mL volumetric flask and diluting to volume with carbon disulfide or another appropriate solvent. The standard and intermediate stock solution will be maintained in glass bottles with PTFE-lined lids in a refrigerator.

3.3 Gasoline Positive Control

The gasoline positive control is a 0.1% (1.0 $\mu\text{L}/\text{mL}$) solution of gasoline in either carbon disulfide or methanol.

A 1% (10.0 $\mu\text{L}/\text{mL}$) intermediate stock solution is prepared by adding 100 μL of neat gasoline to a 10-mL volumetric flask and diluting to volume with carbon disulfide, hexane, or methanol.

A 0.1% (1.0 $\mu\text{L}/\text{mL}$) solution can be prepared by adding 1000 μL of the 1% ppm stock solution to a 10-mL volumetric flask and diluting to volume with carbon disulfide, hexane, or methanol.

The standard and intermediate stock solution will be maintained in glass bottles with PTFE-lined lids in a refrigerator.

3.4 Ignitable Liquids Positive Controls

A variety of ignitable liquids (IL) acquired as known commercial materials are maintained for comparison and classification use both in their neat form and in dilutions ranging from 0.05% to 1% in an appropriate solvent (e.g., methanol, hexane, carbon disulfide).

A 1% solution can be prepared by adding 100 μL of a neat reference material to a 10-mL volumetric flask and diluting to volume with an appropriate solvent.

A 0.5% solution can be prepared by adding 500 μL of a neat reference material to a 100-mL volumetric flask and diluting to volume with an appropriate solvent.

A 0.1% solution can be prepared by adding 100 μL of a neat reference material to a 100-mL volumetric flask and diluting to volume with an appropriate solvent.

A 0.05% solution can be prepared from a 0.5% intermediate stock solution by adding 5 mL of the 0.5% stock solution to a 50-mL volumetric flask and dilute to volume with an appropriate solvent.

Ignitable liquid standards will be maintained in glass bottles with PTFE-lined lids in a refrigerator.

3.5 Charcoal Strips

3.5.1 New lots of charcoal strips are verified for efficacy by extracting a 10 µL gasoline sample in a container using the passive adsorption technique. A blank charcoal strip portion (approximately 0.5 by 1 cm) from the new lot is extracted with carbon disulfide and analyzed to detect any hydrocarbon contamination of the strips prior to casework. Verification data is retained in the verification files.

3.5.2 For each sample batch, a blank charcoal strip portion (approximately 0.5 by 1 cm, from the same lot used for the sample batch) is extracted with carbon disulfide and analyzed as a negative control.

3.6 Extraction/Dilution Solvents

3.6.1 For each sample batch, an aliquot of the solvent used for final extraction or dilution is analyzed as a solvent blank.

3.6.2 When samples are directly extracted with solvent, as directed in section 5.2.2, an equivalent amount of solvent is filtered, evaporated to a volume approximating final sample sizes, and analyzed as a negative control.

3.7 System Blank

3.7.1 Prepare a system blank by placing a new carbon strip portion (approximately 0.5 x 1 cm) into a clean dry evidence container (e.g., metal can, nylon bag) and processing as described in section 5.1 or section 5.2.1.

3.7.2 When appropriate, prepare a system blank each day that questioned samples are processed.

3.7.3 If the results of the system blank indicate that the system blank was contaminated, review the sample results to determine if and how the question sample results were affected. Evaluate the individual components of the system blank to determine possible contamination origin(s). Process and analyze a new system blank prior to resuming casework processing.

4 Sampling

Fire debris and solid items are routinely examined in their entirety. When a destructive technique such as solvent extraction (section 5.2.2) is to be used, a representative portion of a fire debris sample may be selected for analysis.

Less than 1 mL of liquid samples is used for testing. A portion of a liquid item is taken for analysis when the item appears to be homogenous. If the item appears to consist of two or more immiscible layers, then a sample is taken of each liquid layer and examined separately.

5 Procedure

Evidence items should be received in air-tight and vapor-tight containers: paint cans, nylon or polyester bags, or glass jars. Containers not approved for use with evidence to be examined for trace volatiles or ignitable liquids include paper bags, cardboard boxes or tubes, other paper products/containers, film canisters, coffee cans, or any used containers. Evidence packaged in polyethylene bags (zipper-lock or trash bags), some plastic containers, or other questionable containers will be evaluated by the examiner prior to or after the analysis to determine the extent of any contamination related to the packaging. Improperly packaged fire debris will be noted and returned to the contributor without analysis.

Evidence items will be visually inspected and contents noted just prior to and/or after processing. Obvious odors should be noted to assist with the analysis strategy. However, intentional smelling of the evidence is not recommended as it may pose a health risk.

5.1 Passive Adsorption/Elution Technique

The routine analysis of fire debris samples (burned or unburned) for ignitable liquid residues (ILR) involves extraction of the samples using a passive headspace concentration technique with activated charcoal followed by extract analysis with GC/MS.

5.1.1 For cans and glass jars, punch a hole through the lid using a nail. Remove the lid and thread a wire or paper clip with a charcoal strip (approximately 1 cm x 1 cm) attached through the hole. Seal the hole in the lid with tape. The tape also helps keep the wire in place.

5.1.2 Observe the contents of the container before replacing the lid to see that the contents are as described by the contributor. Secure the lid to the container making sure that the charcoal strip, now suspended inside the container, does not touch the contents.

5.1.3 For items in nylon bags, cut open the bag and secure a wire with a charcoal strip inside the bag but without physically contacting the evidence items. Reseal the bag using a heat sealer. If the bag cannot be resealed, then transfer the contents to a new nylon bag or unused metal can along with a charcoal strip.

5.1.4 Heat the container (or nylon bag) in an oven at approximately 80°C for at least three hours. After heating, allow the container to equilibrate to approximately ambient temperature. Heating times and temperatures may be varied depending upon the type of ignitable liquids and the quantity present in each sample.

5.1.5 Open the container in a hood and remove the charcoal strip from the wire. Cut the strip into two pieces and retain one portion in an autosampler vial as secondary evidence. Place the remainder of the strip into a small test tube (~12 x 75 mm) and add approximately 0.3 mL carbon disulfide. Vortex for about 30 seconds then rinse the strip with the carbon disulfide extract repeatedly with the aid of a Pasteur pipette. The extract is then transferred to an autosampler vial and sealed.

5.1.6 Samples are analyzed along with appropriate standards, blanks, gasoline positive controls, and ignitable liquid positive controls by GC/MS in electron ionization (EI) mode.

5.2 Optional Techniques

Samples suspected of containing low-boiling compounds, such as alcohols, may need to be examined using a direct headspace technique. Samples containing heavy petroleum distillates may need to be solvent extracted. Non-aqueous liquid samples may be diluted with solvent and analyzed directly.

5.2.1 Direct Headspace

A portion of sample headspace can be screened on the Headspace GC/MS for volatile compounds, such as simple alcohols and ketones. Small items of evidence may also be screened if the item can fit within a 10 or 20 mL vial. A 0.5 mL sample of the headspace GC/MS volatiles test mix in an autosampler vial serves as a positive control. A sealed blank autosampler vial and/or appropriate system blanks serve as negative control(s). The evidence and appropriate system blanks may be heated up to 90°C, prior to headspace sampling, based on the analyst's judgment on how much heating is necessary and for how long.

Using an air-tight disposable syringe assembly, withdraw 5-10 ml of sample headspace by inserting the syringe needle through the taped hole in the sample can lid (Section 5.1.1) or through the side of a nylon bag container (Section 5.1.3). Inject the headspace sample into a new sealed headspace autosampler vial for GC/MS. Reseal the hole in the evidence container with clear tape. Place the sealed evidence in the oven for further processing.

5.2.2 Solvent Extraction/Rinsing

After performing the passive adsorption/elution or headspace techniques, the sample can be washed with hexane or pentane which will remove any heavy fuels, such as diesel or kerosene. Pour just enough solvent into a clean container (e.g., a beaker) with sample to cover the debris. Agitate or swirl the sample for several minutes. Filter the solvent through filter paper into a clean beaker and concentrate using heat, compressed air, or nitrogen gas as necessary. Transfer the solvent extract to an autosampler vial, seal, and analyze by GC/MS (EI) as described in section 5.1.6.

Non-porous items such as pieces of glass or the inner surfaces of containers that may have held ignitable liquids may be rinsed with a suitable solvent (e.g., pentane, hexane, or carbon disulfide) to remove any ignitable liquid residues. Use the minimum amount of solvent necessary to rinse the appropriate surface. Solvent rinses can be concentrated by reducing the final volume under an air or nitrogen gas stream; however, this can result in the loss of low boiling point compounds.

Upon completion of the analysis, if the sample extract needs to be preserved, a charcoal strip is placed into the autosampler vial to allow the solvent to adsorb onto the strip for long-term storage of the extract.

5.2.3 Liquid Samples

Liquid samples should be tested for hydrophobicity by adding a few drops to an aliquot of deionized water and vortexing to determine if the sample is miscible with water. Liquid samples miscible with water may be analyzed directly by FTIR to determine if the bulk of the sample is consistent with water or an alcohol. Headspace GC/MS can be used to confirm the presence of alcohols and select volatile compounds. For non-aqueous liquid samples, a 0.5% dilution is prepared for analysis by diluting the equivalent of 5 μ L into 1 mL of carbon disulfide.

Liquid samples may be evaluated for their ability to ignite by testing with an open flame. A few drops of the liquid are applied to a new cotton-tipped applicator and an open flame is introduced to the vapors just above the wetted cotton. If no ignition occurs in the vapor phase, then the flame is brought into direct contact with the cotton. Ease of ignition, flame color, and smoke characteristics should be noted.

5.3 Data Interpretation

Data interpretation of the GC/MS results from unknown item(s) will consist of an initial evaluation to determine if the chromatogram and extracted ion profiles exhibit characteristics indicative of potential ignitable liquid residues, followed by comparison with known ignitable liquids analyzed on the instrument acquisition data system or against the National Center for Forensic Science online database. Results will be reported using the ASTM E1618 ignitable liquid classification system whenever possible. Appropriate reference materials, if available, will be analyzed for direct comparison. Ignitable liquids consisting of a single component or mixtures of just a few components will require suitable comparison with a reference standard for retention time and mass spectral agreement.

6 Instrumental Conditions

The following instrumental conditions may be used for this analysis:

6.1 For GC/MS of Liquid Extracts and Dilutions

Method name: FIRE (or equivalent)
Column Type: J&W DB-5ms or Agilent HP-5MS, 0.25 mm diameter, 0.25 μ m film thickness, ~30 m length
Mode: Constant makeup flow
Initial pressure: 9.1 psi
Nominal initial flow: 1.2 mL/min
Carrier gas: Helium
Injection volume: 1.0 μ L
Inlet: Split
Split ratio: 30:1
Solvent delay: 2.5 minutes
Inlet temp: 250°C
Initial temp: 40°C
Initial time: 3 min
Ramp: 15°C/min
Final temp: 265°C
Final time: 5 min
Mass range: 41-400 m/z (EI)

6.2 For GC/MS Analysis of Headspace Vapors

Method name: Volatiles_Split_HS_10mL and Volatiles_Split_HS_20mL (or equivalent)
Incubator: 80°C for 5 min
Injection volume: 1.0 mL from HS syringe at 90°C
Inlet: Split
Split ratio: 10:1
Inlet temp: 150°C
Initial temp: 40°C
Initial time: 4 min
Ramp: 10°C/min
Final temp: 120°C
Ramp 2: 30°C/min
Final temp 2: 250°C
Total run time: 16.333 min
Scan range: 29-400 m/z
Solvent delay: 2 min

Column Type: J&W DB-624, 0.25 mm diameter, 1.4 μ m film thickness, ~30 m length
Mode: Constant makeup flow
Initial pressure: 9.5 psi
Nominal initial flow: 3.7 mL/min
Carrier gas: Helium

6.3 For FTIR Analysis of Liquids and Solids

Most FTIRs include an ATR accessory. Analyses should be performed in ATR mode whenever possible. The ATR accessories may include various focusing lenses such as ZnSe or KRS-5 which allow for different scan limits.

The FTIRs are typically used with the following settings unless otherwise specified in the case notes.

Mode:	Reflectance
Number of scans:	32
Resolution:	4
Scan range:	650-4000 cm^{-1} or greater as allowed by the instrument

7 Decision Criteria

The following criteria are used as guidelines in determining the acceptability of data produced in this procedure.

7.1 Gas Chromatography/Mass Spectrometry

- Peaks should show good chromatographic characteristics with reasonable peak shape, width, and resolution. Resolution should be evaluated prior to conducting any casework on a new instrument or chromatographic column by analyzing a commercial ignitable liquids resolution test mixture and ensuring adequate separation between all components. Resolution should be evaluated for each analytical batch by checking for near baseline separation between the n-octadecane and phytane (2,4,10,16-tetramethylhexadecane) peaks in the SAM chromatogram.
- The retention time of a compound of interest should be within $\pm 2\%$ of the retention time of a contemporaneously analyzed reference material.
- The signal intensity for a peak of interest should be ≥ 10 times the signal intensity for a peak of the same compound present in an injection immediately prior, as well as in the associated Negative Control or System Blank.

7.2 Fourier Transform Infrared Spectrophotometry

- The FTIR spectra from the material of interest should compare favorably to the corresponding Positive Control's spectra (or to library spectra).

8 Calculations

Not applicable.

9 Measurement Uncertainty

Not applicable.

10 Limitations

Burned material from which the samples are extracted may contain many of the same components commonly found in ignitable liquids. The examiner must recognize these interferences during data interpretation. Refer to references listed below for a more detailed understanding of analytical limitations and data interpretation.

11 Safety

Safety protocols, contained within the FBI Laboratory Safety Manual, will be observed at all times.

Standard precautions will be taken for the handling of all chemicals, reagents, and standards including standard universal precautions for the handling of biological and potentially hazardous materials. Refer to the FBI Laboratory Safety Manual for proper handling and disposal of all chemicals. Personal protective equipment will be used when handling any chemical and when performing any type of analysis.

12 References

FBI Laboratory Quality Assurance Manual

FBI Laboratory Operations Manual

FBI Laboratory Safety Manual

FBI Laboratory Chemistry Unit Quality Assurance and Operations Manual

FBI Laboratory Explosives Unit Quality Assurance Manual

Instrument Operations Manuals for the specific models and accessories used.

Ignitable Liquids Database, National Center for Forensic Science, <http://ilrc.ucf.edu/>.

ASTM Method E 1386, *Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Solvent Extraction*.

ASTM Method E 1388, *Standard Practice for Sampling of Headspace Vapors from Fire Debris Samples*.

ASTM Method E 1412, *Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration With Activated Charcoal*.

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

ASTM Method E 2451, *Standard Practice for Preserving Ignitable Liquids and Ignitable Liquid Residue Extracts from Fire Debris Samples*.

Evans-Nguyen, K. and Hutches, K. (Ed.), *Forensic Analysis of Fire Debris and Explosives*, Springer Nature, Switzerland AG, 2019.

Hendrikse, J., Grutters, M., Schäfer, F. *Identifying Ignitable Liquids in Fire Debris. A Guideline for Forensic Experts*. Academic Press, 2016.

Kelly, R. L., and Martz, R. M., *Accelerant Identification in Fire Debris by Gas Chromatography/Mass Spectrometry Techniques*, Journal of Forensic Sciences, Vol. 29, No. 3, July 1984, pp. 714-722.

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

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0	07/15/2020	New CU SOP resulting from transfer of procedure from EU.

Approval

Redacted - Signatures on File

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