

## Validation Report for Fire Debris Analysis by GC-MS

### Purpose/Scope

This report describes the validation to identify ignitable liquids in fire debris, unknown liquids and solid materials by GC-MS. Passive Headspace Concentration with Activated Charcoal Strips, Solvent Extraction and Liquid Sample Dilution are the sample preparation techniques to be evaluated. The validation was performed to confirm that the techniques described in the Chemistry Unit Fire Debris SOPs are suitable for their intended use.

### Performance Characteristics

Characteristics to be evaluated are Precision/Repeatability, Sensitivity/Limit of Detection, Carry Over, Selectivity/Matrix Effect and Robustness.

### Instrumental Parameters

PARAMETERS/CONDITIONS	GC-MS #6
Instrument	Agilent 7890B GC / 5977B MSD
Method	FIRE.M
Software	Mass Hunter
<b>INJECTION</b>	
Type	Autosampler 7693
Split Ratio	20:1
Injection Volume	1.0 µl
Injector Temperature	250 °C
Split Flow	24 mL/minute
Total Flow	28.2 mL/minute
Gas Saver Flow	30 mL/minute
Gas Saver Time	3 minutes
<b>AUTOSAMPLER</b>	
Sample Washes	1
Sample Pumps	2
Syringe Size	10 mL
Post Injection solvent A washes	5
Solvent A	pentane
Post Injection solvent B washes	5
Solvent B	pentane
Plunger Speed	fast
<b>COLUMN</b>	
Column type	DB-1MS (30m x 0.25mm internal diameter x 0.25µm film)
Carrier gas	High Purity Helium
Flow	1.2 ml/min
<b>OVEN</b>	

Initial Temperature	35 °C for 2.5 minutes
Ramp	15 °C/minute to 300 °C
Final Temperature	300 °C for 5.5 minutes
Total run time	25.667 minutes
<b>MASS SPECTROMETER</b>	
Detector	MS Quadrupole
Detector Temperature	150 °C
Source Temperature	230 °C
Transfer Line Temperature	280 °C
Timed event 1	Detector ON at 0.00 minutes
Scan Range 1 (starting at 0.00 min)	15 – 85 m/z
Timed event 2	Detector OFF at 1.65 minutes
Timed event 3	Detector ON at 2.17 minutes
Scan Range 2 (starting at 2.18 min)	33 – 400 m/z
Threshold	100
Tune file	Atune.u
EM Setting	Gain factor 1.0

Note: Timed events 2 and 3 were adjusted as necessary, to avoid solvent detection, after instrument maintenance.

## Reference Materials

PFTBA, used to calibrate the MS

E1618-97 Test Mixture, purchased from Restek, lot # A0122285

n-Hydrocarbon Standard C6-C28, purchased from Absolute Standards, lot # 032114

Tetrachloroethylene, used as Internal Standard (IS), purchased from Alfa Aesar, lot # 10206615

In-house reference ignitable liquids

## Procedure

### 1. Precision/Repeatability

#### Day 1

Inject four (4) times an E1618-97 test mixture containing even-numbered of normal alkanes (from hexane to eicosane), toluene, p-xylene (1,4-dimethylbenzene), m-ethyltoluene (1-methyl-3-ethylbenzene), o-ethyltoluene (1-methyl-2-ethylbenzene), and 1,2,4-trimethylbenzene, diluted with carbon disulfide (CS<sub>2</sub>) to a final concentration of 0.005% volume/volume (v/v) for each component, on the GC-MS. The test mixture will also contain ethanol and acetone at a concentration of 0.05% v/v.

Inject four (4) times a n-hydrocarbon standard C6-C28 diluted with CS<sub>2</sub> to a final concentration of 50 ug/mL for each component on the GC-MS.

Day 2

Inject the test mixture and the n-hydrocarbon standard three (3) times. Retention times shall be  $\pm 0.05$  minute from previous day retention times for each component.

Day 3

Inject the test mixture and the n-hydrocarbon standard three (3) times. Retention times shall be  $\pm 0.05$  minute from previous day retention times for each component.

On each day print chromatograms, including retention time (RT) of each component. The acceptance criteria for the injections are baseline separation of all peaks, symmetrical peak shape, and a range of  $\pm 0.05$  minute average RT for each component. For the test mixture print the head to tail NIST search spectrum for each component (only for the first injection of each day). For the n-hydrocarbon standard print the head to tail NIST search spectrum for the odd-numbered n-alkanes and for those even-numbered n-alkanes not present in the test mixture (only for the first injection of each day) (match factor shall be  $\geq 800$ ).

Upon completion of the three-day procedure, evaluate the within-run precision and between-run precision. Within-run precision is determined by calculating the coefficient of variation (CV) for the replicate measurements (retention time) for each day. Between-run precision is determined by calculating the CV for the mean of the replicate measurements for day 1, day 2 and day 3. (CV shall be  $\leq 5\%$ ).

Note: The E1618-97 test mixture shall be injected every day of instrument use. Retention times shall be  $\pm 0.05$  minute from previous day retention times for each component.

2. Sensitivity/Limit of Detection (LOD)

Choose a reference ignitable liquid (IL) representative of the classes/sub-classes gasoline, light petroleum distillates (LPD), medium petroleum distillates (MPD), heavy petroleum distillates (HPD), isoparaffinic products, aromatic products, naphthenic-paraffinic products, normal-alkanes products, oxygenated solvents, and other-miscellaneous. Use Table 1 to prepare nine solutions of each IL. Use an internal standard (IS) of 25 ppm of tetrachloroethylene (perchloroethylene or PCE) in CS<sub>2</sub> as diluent.

Table 1. IL solutions for LOD

Soln #	Initial volume (uL)	Source	Final volume (uL)	Final [ ] (%v/v)
1	10	IL	1000	1
2	2	IL	2000	0.1
3	500	Soln 2	1000	0.05
4	100	Soln 2	1000	0.01
5	50	Soln 2	1000	0.005
6	10	Soln 2	1000	0.001
7	50	Soln 4	1000	0.0005

8	10	Soln 4	1000	0.0001
9	5	Soln 4	1000	0.00005

Run the nine solutions on the GC-MS on day 1. Rerun the nine solutions on day 2 and day 3. Solutions at levels that were not detectable on day 1 do not have to be repeated. Print chromatograms and extracted ion profiles for alkanes, aromatics, cycloalkanes, polynuclear aromatics and indanes. Those ions are listed in Table 5. Determine the LOD, which is defined as the lowest concentration where the IL peaks pattern can be recognized from the background or baseline and properly identified. The GC-MS shall detect at least the 0.005% v/v solution for each IL.

### 3. Carry Over

Analyze a blank (IS) after each solution of highest concentration (1% v/v) for LOD determination. Print chromatograms and extracted ion profiles. Injections shall demonstrate the absence of carryover.

### 4. Selectivity/Matrix Effect

Analyze fourteen (14) samples, including positives (containing an IL) and negatives (matrix only), for each analytical technique to be validated. Positive samples, mixed with potential interfering substances, should include at least one example representative of the classes/sub-classes gasoline, LPD, MPD, HPD, isoparaffinic products, aromatic products, naphthenic-paraffinic products, normal-alkanes products, oxygenated solvents, and other-miscellaneous. This step should prove the ability of the procedure to differentiate unequivocally the analyte in the presence of other components in the sample. Print chromatograms and extracted ion profiles. Each IL shall be identified in its proper class with all analytical techniques used. Use the identification criteria described in section 10 (Ignitable Liquid Classification Scheme) of the ASTM E1618-14. No IL shall be detected in negative (matrix only) samples.

#### 4.1 Passive Headspace Concentration (PHSC) with Activated Charcoal Strips (ACS)

Place a small amount of fire debris or piece of cloth inside either a metal can or a nylon arson evidence bag. Add an ignitable liquid (50  $\mu$ L) to the matrix, or nothing, as applicable. Suspend half of an ACS using dental floss and a paperclip (for cans) or place a test tube containing an ACS held close to the top with a paperclip (for bags). Seal the container. Heat the container overnight (for about 16 hours) in an oven at 65°C. After allowing the container to cool to room temperature, remove the ACS and desorb it with a minimum amount (about 0.5 mL) of IS (25 ppm of PCE in CS<sub>2</sub>) for GC-MS analysis. Analyze the proper blanks. Use Table 2 as a guide to prepare the samples.

Table 2. PHSC samples for Selectivity

Sample #	Container	Matrix	IL class
H1	can	fire debris (synthetic material)	none
H2	can	fire debris (natural material)	gasoline
H3	bag	cloth (unburned)	LPD
H4	bag	cloth (partially burned)	none
H5	can	fire debris (synthetic material)	MPD
H6	can	cloth (unburned)	oxygenated solvent
H7	bag	fire debris (natural material)	isoparaffinic product
H8	can	fire debris (synthetic material)	normal-alkanes product
H9	can	cloth (unburned)	none
H10	bag	fire debris (natural material)	HPD
H11	bag	fire debris (synthetic material)	others-miscellaneous
H12	can	fire debris (natural material)	aromatic product
H13	can	fire debris (natural material)	none
H14	bag	cloth (partially burned)	naphthenic-paraffinic product

#### 4.2 Solvent Extraction

Place a small amount of glass, cloth, plastic or wood inside either a metal can or a nylon arson evidence bag. Add an ignitable liquid (30 uL) to the matrix, or nothing, as applicable. Seal the container (can or bag). After at least one day open the container and transfer part of the sample into an appropriate sized clean glass beaker or other suitable container. Add sufficient IS (25 ppm of PCE in pentane) to thoroughly saturate the sample. After an extraction time of about 30 seconds, decant the solvent (and filter, if necessary) into a clean container. Concentrate the extract using nitrogen or air and analyze by GC-MS. Analyze the proper extraction blanks. Use Table 3 as a guide to prepare the samples.

Table 3. Solvent Extraction samples for Selectivity

Sample #	Container	Matrix	IL class
E1	can	glass pieces	none
E2	can	cloth pieces	gasoline
E3	bag	plastic pieces	LPD
E4	bag	wood pieces	none
E5	can	wood pieces	MPD
E6	can	plastic pieces	naphthenic-paraffinic product
E7	bag	glass pieces	isoparaffinic product
E8	can	wood pieces	normal-alkanes product
E9	can	plastic pieces	none
E10	bag	glass pieces	HPD
E11	bag	cloth pieces	others-miscellaneous
E12	can	plastic pieces	aromatic product
E13	can	glass pieces	oxygenated solvent
E14	bag	cloth pieces	none

### 4.3 Liquid Sample Dilution

Dilute 1.5 microliters of different liquids, including positive (IL) and negative (non IL) with 1.5 mL of IS (25 ppm of PCE in CS<sub>2</sub>) and analyze by GC-MS. Perform miscibility and flame tests to each liquid. Use Table 4 as a guide to prepare the samples.

Table 4. Liquid samples for Selectivity

Sample #	Composition
L1	gasoline
L2	water
L3	LPD
L4	HPD
L5	MPD
L6	naphthenic-paraffinic product
L7	isoparaffinic product
L8	normal-alkanes product
L9	cooking oil
L10	gasoline:water (50:50)
L11	others-miscellaneous
L12	aromatic product
L13	oxygenated solvent
L14	dish soap

### 4.4 SIM

Select fourteen (14) samples with high matrix interference from sections 4.1 and 4.2 (autosampler vial - seven from each section), including negatives, and re-analyze them using SIM Fire method. This method has the same parameters/conditions of Fire method but has a solvent delay of 2.17 minutes and performs a selected ion monitoring (SIM) instead of performing a full scan. Table 5 includes the selected ions.

Table 5. Selected ions for SIM Fire method.

Class	Ions			
Alkanes	57	71	85	99
Aromatics	91	105	119	
Cycloalkanes	55	69	83	
Polynuclear aromatics	128	142	156	
Indanes	117	118	131	132

## 5. Robustness

Analyze fourteen (14) samples, including positives (containing an IL) and negatives (matrix only), for PHSC with ACS and Solvent Extraction techniques. Prepare samples as described in

sections 4.1 and 4.2 but introduce some procedural variations (different adsorption time, adsorption temperature and/or concentration technique). Print chromatograms and extracted ion profiles. Each IL shall be identified in its proper class with all analytical techniques used. Use the identification criteria described in section 10 (Ignitable Liquid Classification Scheme) of the ASTM E1618-14. No IL shall be detected in negative (matrix only) samples. This step should prove the capacity of the method to maintain suitability for intended use by deliberate variations in procedural parameters.

### 5.1 Passive Headspace Concentration with Activated Charcoal Strips

Place a small amount of fire debris or piece of cloth inside either a metal can or a nylon arson evidence bag. Add an ignitable liquid (50  $\mu$ L) to the matrix, or nothing, as applicable. Suspend half of an ACS using dental floss and a paperclip (for cans) or place a test tube containing an ACS held close to the top with a paperclip (for bags). Seal the container. Follow the adsorption time/temperature described in Table 6. After allowing the container to cool to room temperature (when applicable), remove the ACS and desorb it with a minimum amount (about 0.5 mL) of IS (25 ppm of PCE in  $CS_2$ ) for GC-MS analysis. Analyze the proper blanks.

Table 6. PHSC samples for Robustness

Sample #	Container	Matrix	IL class	Variation in adsorption
R1	can	fire debris (synthetic material)	none	16 hrs @ 85°C
R2	can	fire debris (natural material)	HPD	16 hrs @ 85°C
R3	bag	cloth (unburned)	LPD	16 hrs @ 55°C
R4	bag	cloth (partially burned)	none	16 hrs @ 55°C
R5	can	fire debris (synthetic material)	MPD	16 hrs @ 35°C
R6	can	cloth (unburned)	oxygenated solvent	16 hrs @ room temperature
R7	bag	fire debris (natural material)	isoparaffinic product	16 hrs @ room temperature
R8	can	fire debris (synthetic material)	normal-alkanes product	0.5 hrs @ 65°C
R9	can	cloth (unburned)	none	0.5 hrs @ 65°C
R10	bag	fire debris (natural material)	gasoline	4 hrs @ 65°C
R11	bag	fire debris (synthetic material)	others-miscellaneous	4 hrs @ 65°C
R12	can	fire debris (natural material)	aromatic product	8 hrs @ 65°C
R13	can	fire debris (natural material)	none	25 hrs @ 65°C
R14	bag	cloth (partially burned)	naphthenic-paraffinic product	25 hrs @ 65°C

### 5.2 Solvent Extraction

Place a small amount of glass, cloth, plastic or wood inside either a metal can or a nylon arson evidence bag. Add an ignitable liquid (30 uL) to the matrix and seal the container (can or bag). After at least one day open the container and transfer the sample into an appropriate sized clean glass beaker or other suitable container. Add sufficient solvent (25 ppm of PCE in pentane) to thoroughly saturate the sample. After an extraction time of about 60 seconds, decant the solvent (and filter, if necessary) into a clean container. Concentrate the extract by letting the solvent to partially evaporate at room temperature and analyze by GC-MS. Analyze the proper blanks. Use Table 7 as a guide to prepare the samples.

Table 7. Solvent Extraction samples for Robustness

Sample #	Container	Matrix	IL class
S1	can	glass pieces	none
S2	can	cloth pieces	gasoline
S3	bag	plastic pieces	LPD
S4	bag	wood pieces	none
S5	can	wood pieces	MPD
S6	can	plastic pieces	naphthenic-paraffinic product
S7	bag	glass pieces	isoparaffinic product
S8	can	wood pieces	normal-alkanes product
S9	can	plastic pieces	none
S10	bag	glass pieces	HPD
S11	bag	cloth pieces	others-miscellaneous
S12	can	plastic pieces	aromatic product
S13	can	glass pieces	oxygenated solvent
S14	bag	cloth pieces	none

## Results

### 1. Precision/Repeatability

Table 8. E1618 + Ethanol/Acetone Test Mixture Injections Results

Component	Average RT $\pm$ range (minutes)			Precision (%CV)	
	Day 1	Day 2	Day 3	Within-Run (max)	Between-Run
Ethanol	1.55 $\pm$ 0.00	1.55 $\pm$ 0.00	1.55 $\pm$ 0.00	0.00	0.00
Acetone	1.61 $\pm$ 0.00	1.61 $\pm$ 0.00	1.61 $\pm$ 0.00	0.00	0.00
Hexane	2.25 $\pm$ 0.00	2.25 $\pm$ 0.00	2.25 $\pm$ 0.00	0.00	0.00
Toluene	4.29 $\pm$ 0.00	4.29 $\pm$ 0.01	4.29 $\pm$ 0.01	0.13	0.09
Octane	5.02 $\pm$ 0.00	5.02 $\pm$ 0.00	5.02 $\pm$ 0.00	0.00	0.00
p-xylene	5.86 $\pm$ 0.00	5.86 $\pm$ 0.00	5.86 $\pm$ 0.00	0.00	0.00
m-ethyltoluene	7.11 $\pm$ 0.01	7.11 $\pm$ 0.01	7.10 $\pm$ 0.00	0.08	0.01
o-ethyltoluene	7.32 $\pm$ 0.00	7.32 $\pm$ 0.00	7.32 $\pm$ 0.00	0.00	0.00
1,2,4-TMB	7.51 $\pm$ 0.00	7.51 $\pm$ 0.00	7.51 $\pm$ 0.00	0.00	0.00
Decane	7.75 $\pm$ 0.00	7.75 $\pm$ 0.00	7.75 $\pm$ 0.00	0.00	0.00
Dodecane	9.92 $\pm$ 0.00	9.92 $\pm$ 0.00	9.92 $\pm$ 0.00	0.00	0.00
Tetradecane	11.78 $\pm$ 0.01	11.77 $\pm$ 0.00	11.77 $\pm$ 0.01	0.05	0.02



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Hexadecane	13.42 ± 0.00	13.42 ± 0.00	13.42 ± 0.00	0.00	0.00
Octadecane	14.89 ± 0.00	14.89 ± 0.00	14.89 ± 0.00	0.00	0.00
Eicosane	16.23 ± 0.00	16.23 ± 0.00	16.23 ± 0.00	0.00	0.00

Table 9. Hydrocarbon Standard Injections Results

Component	Average RT ± range (minutes)			Precision (%CV)	
	Day 1	Day 2	Day 3	Within-Run (max)	Between-Run
Hexane	2.26 ± 0.01	2.25 ± 0.00	2.25 ± 0.00	0.22	0.19
Heptane	3.48 ± 0.00	3.48 ± 0.00	3.48 ± 0.01	0.17	0.06
Octane	5.02 ± 0.00	5.02 ± 0.00	5.02 ± 0.00	0.00	0.00
Nonane	6.47 ± 0.00	6.47 ± 0.00	6.47 ± 0.00	0.00	0.00
Decane	7.75 ± 0.00	7.75 ± 0.00	7.75 ± 0.00	0.00	0.00
Undecane	8.89 ± 0.00	8.89 ± 0.00	8.89 ± 0.00	0.00	0.00
Dodecane	9.92 ± 0.00	9.92 ± 0.00	9.92 ± 0.00	0.00	0.00
Tridecane	10.88 ± 0.00	10.88 ± 0.00	10.88 ± 0.00	0.00	0.00
Tetradecane	11.77 ± 0.01	11.77 ± 0.01	11.77 ± 0.01	0.05	0.00
Pentadecane	12.62 ± 0.00	12.62 ± 0.00	12.62 ± 0.00	0.00	0.00
Hexadecane	13.42 ± 0.00	13.42 ± 0.00	13.42 ± 0.00	0.00	0.00
Heptadecane	14.17 ± 0.00	14.17 ± 0.00	14.17 ± 0.00	0.00	0.00
Octadecane	14.89 ± 0.00	14.89 ± 0.00	14.89 ± 0.00	0.00	0.00
Nonadecane	15.57 ± 0.00	15.57 ± 0.00	15.57 ± 0.00	0.00	0.00
Eicosane	16.23 ± 0.00	16.23 ± 0.00	16.23 ± 0.00	0.00	0.00
Heneicosane	16.85 ± 0.00	16.85 ± 0.00	16.85 ± 0.00	0.00	0.00
Docosane	17.44 ± 0.00	17.44 ± 0.00	17.44 ± 0.00	0.00	0.00
Tricosane	18.01 ± 0.00	18.01 ± 0.00	18.01 ± 0.00	0.00	0.00
Tetracosane	18.56 ± 0.00	18.56 ± 0.00	18.56 ± 0.00	0.00	0.00
Pentacosane	19.09 ± 0.00	19.09 ± 0.00	19.09 ± 0.00	0.00	0.00
Hexacosane	19.59 ± 0.00	19.59 ± 0.00	19.59 ± 0.00	0.00	0.00
Heptacosane	20.08 ± 0.00	20.08 ± 0.00	20.08 ± 0.00	0.00	0.00
Octacosane	20.57 ± 0.00	20.57 ± 0.00	20.57 ± 0.00	0.00	0.00

Table 10. Precision/Repeatability Compliance with Acceptance Criteria

Criteria (for each component)	E1618 Test Mixture	Hydrocarbon Standard
Range ± 0.05 minute from average RT	yes	yes
RT ± 0.05 minute from previous day RT	yes	yes
NIST match factor ≥ 800	yes	yes
Within-Run and Between-Run CV ≤ 5%	yes	yes
Symmetrical peak shape, baseline separation	yes	yes

2. Sensitivity/Limit of Detection (LOD)

Table 11. LOD Determination Results

IL Class (Sub-class)	Ref #	Description	LOD (% v/v)
Gasoline	71	93 Octane Shell Gasoline	0.005
Petroleum Distillates (Light)	16	Zippo Lighter Fluid	0.005

Petroleum Distillates (Medium)	13	Jasco Paint Thinner	0.001
Petroleum Distillates (Heavy)	22	Shell Diesel	0.005
Normal-Alkanes Products (Heavy)	12	Lamplight Lamp Oil	0.0005
Aromatic Products (Light)	7	Goof Off Paint Remover	0.005
Isoparaffinic Products (Medium)	156	CRC Multi-purpose Power Lube	0.005
Naphthenic-Paraffinic Products (Heavy)	33	Tiki Torch Fuel	0.005
Other-Miscellaneous (Medium)	147	Klean Strip Spirits Turpentine	0.001
Oxygenated Solvents (Light)	191	Klean Strip Green Lacquer Thinner	0.05

### 3. Carry Over

Blank (IS) injections after each solution of highest concentration (1% v/v) for LOD determination demonstrated absence of carryover.

### 4. Selectivity/Matrix Effect

#### 4.1 Passive Headspace Concentration (PHSC) with Activated Charcoal Strips (ACS)

Table 12. PHSC with ACS Selectivity/Matrix Effects Results

Sample #	IL added	Alkanes	Cycloalkanes	Aromatics	Polynuclear Aromatics	IL detected	Comments
H1	none	present	present	abundant	present	none	no recognized pattern, burned synthetic material
H2	gasoline	present, less abundant than aromatics	present, less abundant than aromatics	abundant	present	gasoline	distinctive aromatic pattern
H3	LPD	abundant, spiking peaks of n-alkanes (C7–C9)	present, less abundant than alkanes	present, less abundant than alkanes	present, less abundant than alkanes	LPD	pattern between C6 and C10
H4	none	not present in significant amounts	not present in significant amounts	not present in significant amounts	naphthalene	none	partially burned cloth
H5	MPD	abundant, Gaussian distribution	present, less abundant than alkanes	present, less abundant than alkanes	present, less abundant than alkanes	MPD	spiking peaks of n-alkanes (C9–C12)

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H6	OS(L)	not present in significant amounts	not present in significant amounts	present, less abundant than oxygenated compounds	not present in significant amounts	OS(L)	ethanol, acetone, ethyl acetate and 2-butoxy-ethanol present
H7	IP(M)	abundant branch alkanes	absent, peaks in EIP are not cycloalkanes	absent	absent	IP(M)	pattern between C11 and C14, terpenes present as in matrix
H8	NA(H)	abundant n-alkanes	absent	present (as in matrix)	present (as in matrix)	NA(H)	C13–C15
H9	none	not present in significant amounts	not present in significant amounts	absent	not present in significant amounts	none	low level of C15 to C18 but below LOD
H10	HPD	abundant, Gaussian distribution	present, less abundant than alkanes	present, less abundant than alkanes	present, less abundant than alkanes	HPD	pattern between C8 and C17
H11	OM(M)	present (as in matrix)	present (as in matrix)	present (as in matrix)	present (as in matrix)	OM(M)	Camphene, D-Limonene, $\gamma$ -terpinene and other terpenes present; pattern between C9 and C13
H12	AP(L)	not present in significant amounts	absent, peaks in EIP are not cycloalkanes	abundant (C2 alkyl-benzenes)	not present in significant amounts	AP(L)	pattern between C8 and C9
H13	none	absent	absent	absent	absent	none	terpenes present, matrix contains wood
H14	NP(H)	abundant, n-alkanes absent	abundant, with spiking peaks	absent	present (as in matrix)	NP(H)	pattern between C9 and C15

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(L)=Light, (M)=Medium, (H)=Heavy, PD=Petroleum Distillate, AP=Aromatic Product, IP=Isoparaffinic Product, NA=Normal-Alkanes Product, NP= Naphthenic-Paraffinic Product, OM= Others-Miscellaneous, OS= Oxygenated Solvent

### 4.2 Solvent Extraction

Table 13. Solvent Extraction Selectivity/Matrix Effects Results

Sample #	IL added	Alkanes	Cycloalkanes	Aromatics	Polynuclear Aromatics	IL detected	Comments
E1	none	not present in significant amounts	not present in significant amounts	absent	absent	none	glass pieces
E2	gasoline	present, less abundant than aromatics	present, less abundant than aromatics	abundant	present	gasoline (weathered)	no peaks in C6-C8 range
E3	LPD	abundant, spiking peaks of n-alkanes (C7-C9)	present, less abundant than alkanes	not present in significant amounts	absent	LPD	pattern between C6 and C10
E4	none	not present in significant amounts	not present in significant amounts	absent	not present in significant amounts	none	wood pieces
E5	MPD	abundant, Gaussian distribution	present, less abundant than alkanes	present, less abundant than alkanes	present, less abundant than alkanes	MPD	spiking peaks of n-alkanes (C9-C12)
E6	NP(H)	abundant, n-alkanes absent	abundant, with spiking peaks	absent	absent	NP(H)	pattern between C9 and C15
E7	IP(M)	abundant branch alkanes	absent	absent	absent	IP(M)	pattern between C11 and C14
E8	NA(H)	abundant n-alkanes	absent	absent	absent	NA(H)	C13-C16
E9	none	not present in significant amounts	not present in significant amounts	absent	absent	none	plastic pieces

E10	HPD	abundant, Gaussian distribution	present, less abundant than alkanes	present, less abundant than alkanes	present, less abundant than alkanes	HPD	pattern between C9 and C24
E11	OM(M)	absent, peaks seen in profile are not alkanes	absent, peaks seen in profile are not cycloalkanes	present, not recognized pattern	not present in significant amounts	OM(M)	Camphene, D-Limonene, $\gamma$ -terpinene and other terpenes present; pattern between C9 and C13
E12	AP(L)	not present in significant amounts	not present in significant amounts	abundant (C2 alkyl-benzenes)	absent	AP(L)	pattern between C8 and C9
E13	OS(L)	absent	absent	absent	absent	none	no peaks
E14	none	absent, peaks seen in profile are not alkanes	absent, peaks seen in profile are not cycloalkanes	absent, peaks seen in profile are not aromatics	absent	none	cloth pieces

(L)=Light, (M)=Medium, (H)=Heavy, PD=Petroleum Distillate, AP=Aromatic Product, IP=Isoparaffinic Product, NA=Normal-Alkanes Product, NP=Naphthenic-Paraffinic Product, OM= Others-Miscellaneous, OS= Oxygenated Solvent

### 4.3 Liquid Sample Dilution

Table 14. Liquid Sample Dilution Selectivity/Matrix Effects Results

Sample #	IL	Alkanes	Cycloalkanes	Aromatics	Polynuclear Aromatics	IL detected	Comments
L1	gasoline	present, less abundant than aromatics	present, less abundant than aromatics	abundant	present	gasoline	distinctive aromatic pattern
L2	water	absent	absent	absent	absent	none	no peaks
L3	LPD	abundant, spiking peaks of n-alkanes (C7-C9)	present, less abundant than alkanes	present, less abundant than alkanes	present, less abundant than alkanes	LPD	pattern between C6 and C10
L4	HPD	abundant, Gaussian distribution	present, less abundant than alkanes	present, less abundant than alkanes	present, less abundant than alkanes	HPD	pattern between C9 and C24

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L5	MPD	abundant, Gaussian distribution	present, less abundant than alkanes	present, less abundant than alkanes	present, less abundant than alkanes	MPD	spiking peaks of n-alkanes (C9–C12)
L6	NP(H)	abundant, n-alkanes absent	abundant, with spiking peaks	absent	absent	NP(H)	pattern between C9 and C15
L7	IP(M)	abundant branch alkanes	absent	absent	absent	IP(M)	pattern between C11 and C14
L8	NA(H)	abundant n-alkanes	absent	absent	absent	NA(H)	C13–C16
L9	cooking oil	absent	absent	absent	absent	none	no significant peaks
L10 (top layer)	gasoline	present, less abundant than aromatics	present, less abundant than aromatics	abundant	present	gasoline	distinctive aromatic pattern
L10 (bottom layer)	water	present, less abundant than aromatics	not present in significant amounts	abundant	not present in significant amounts	gasoline (from contact with top layer)	distinctive aromatic pattern
L11	OM(M)	absent, peaks seen in profile are not alkanes	absent, peaks seen in profile are not cycloalkanes	absent, peaks seen in profile are not aromatics	absent, peaks seen in profile are not polynuclear aromatics	OM(M)	Camphene, D-Limonene, $\gamma$ -terpinene and other terpenes present; pattern between C9 and C11
L12	AP(L)	absent	absent	abundant (C2 alkyl-benzenes)	absent	AP(L)	pattern between C8 and C9
L13	OS(L)	absent	absent	low level of C2 alkyl-benzenes, less abundant than oxygenated compounds	absent	OS(L)	ethanol, acetone, ethyl acetate and 2-butoxy-ethanol present
L14	dish soap	absent	absent	absent	absent	none	no significant peaks

(L)=Light, (M)=Medium, (H)=Heavy, PD=Petroleum Distillate, AP=Aromatic Product, IP=Isoparaffinic Product, NA=Normal-Alkanes Product, NP= Naphthenic-Paraffinic Product, OM= Others-Miscellaneous, OS= Oxygenated Solvent

## 4.4 SIM

Table 15. SIM Method Selectivity/Matrix Effects Results

Sample #	IL added	IL detected – Fire method	IL detected – SIM method	Comments
H1	none	none	none	similar EIPs
H2	gasoline	gasoline	gasoline	similar EIPs
H5	MPD	MPD	MPD	similar EIPs
H8	NA(H)	NA(H)	NA(H)	similar EIPs
H10	HPD	HPD	HPD	similar EIPs
H12	AP(L)	AP(L)	AP(L)	similar EIPs
H13	none	none	none	similar EIPs
E2	gasoline	gasoline	gasoline	similar EIPs
E5	MPD	MPD	MPD	similar EIPs
E8	NA(H)	NA(H)	NA(H)	similar EIPs
E9	none	none	none	similar EIPs
E10	HPD	HPD	HPD	similar EIPs
E12	AP(L)	AP(L)	AP(L)	similar EIPs
E14	none	none	none	similar EIPs

(L)=Light, (M)=Medium, (H)=Heavy, PD=Petroleum Distillate, AP=Aromatic Product, IP=Isoparaffinic Product, NA=Normal-Alkanes Product, NP= Naphthenic-Paraffinic Product, OM= Others-Miscellaneous, OS= Oxygenated Solvent, EIP=Extracted Ion Profile

## 5. Robustness

## 5.1 Passive Headspace Concentration with Activated Charcoal Strips

Table 16. PHSC with ACS Robustness Results

Sample #/ Adsorption	IL added	Alkanes	Cycloalkanes	Aromatics	Polynuclear Aromatics	IL detected	Comments
R1 16 hrs @ 85°C	none	present	present	abundant	present	none	no recognized pattern, burned synthetic material
R2 16 hrs @ 85°C	HPD	abundant, Gaussian distribution	present, less abundant than alkanes	present, less abundant than alkanes	present, less abundant than alkanes	HPD	pattern between C9 and C19
R3 16 hrs @ 55°C	LPD	abundant, spiking peaks of n-alkanes (C7–C9)	present, less abundant than alkanes	present, less abundant than alkanes	present, less abundant than alkanes	LPD	pattern between C6 and C10

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R4 16 hrs @ 55°C	none	not present in significant amounts	not present in significant amounts	not present in significant amounts	naphthalene	none	partially burned cloth
R5 16 hrs @ 35°C	MPD	abundant, Gaussian distribution	present, less abundant than alkanes	present, less abundant than alkanes	present, less abundant than alkanes	MPD	spiking peaks of n- alkanes (C9–C12)
R6 16 hrs @ RT	OS(L)	not present in significant amounts	not present in significant amounts	present, less abundant than oxygenated compounds	not present in significant amounts	OS(L)	ethanol, acetone, ethyl acetate and 2- butoxy- ethanol present
R7 16 hrs @ RT	IP(M)	abundant branch alkanes	absent	not present in significant amounts	not present in significant amounts	IP(M)	pattern between C11 and C14
R8 0.5 hrs @ 65°C	NA(H)	abundant n-alkanes	absent	present (as in matrix)	present (as in matrix)	NA(H)	C13–C15, less abundant than matrix components
R9 0.5 hrs @ 65°C	none	absent	absent	absent	absent	none	basically no peaks
R10 4 hrs @ 65°C	gasoline	present, less abundant than aromatics	present, less abundant than aromatics	abundant	present	gasoline	distinctive aromatic pattern
R11 4 hrs @ 65°C	OM(M)	present (as in matrix)	present (as in matrix)	present (as in matrix)	present (as in matrix)	OM(M)	Terpenes present; pattern between C8 and C13
R12 8 hrs @ 65°C	AP(L)	not present in significant amounts	not present in significant amounts	abundant (C2 alkyl- benzenes)	not present in significant amounts	AP(L)	pattern between C8 and C9
R13 25 hrs @ 65°C	none	absent	absent	absent	absent	none	terpenes present, matrix contains wood
R14 25 hrs @ 65°C	NP(H)	abundant, n-alkanes absent	abundant, with spiking peaks	absent	present (as in matrix)	NP(H)	pattern between C9 and C15



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(L)=Light, (M)=Medium, (H)=Heavy, PD=Petroleum Distillate, AP=Aromatic Product, IP=Isoparaffinic Product, NA=Normal-Alkanes Product, NP= Naphthenic-Paraffinic Product, OM= Others-Miscellaneous, OS= Oxygenated Solvent

### 5.2 Solvent Extraction

Table 17. Solvent Extraction Robustness Results

Sample #	IL added	Alkanes	Cycloalkanes	Aromatics	Polynuclear Aromatics	IL detected	Comments
S1	none	absent	absent	absent	absent	none	glass pieces
S2	gasoline	present, less abundant than aromatics	present, less abundant than aromatics	abundant	present	gasoline (weathered)	no peaks in C6-C9 range
S3	LPD	abundant, spiking peaks of n-alkanes (C7-C9)	present, less abundant than alkanes	absent	absent	LPD	pattern between C6 and C10
S4	none	absent	absent	absent	absent	none	wood pieces
S5	MPD	present in low levels, Gaussian distribution	present, less abundant than alkanes	present, less abundant than alkanes	present, less abundant than alkanes	MPD	spiking peaks of n-alkanes (C10-C12)
S6	NP(H)	abundant, n-alkanes absent	abundant, with spiking peaks	absent	absent	NP(H)	pattern between C9 and C15
S7	IP(M)	abundant branch alkanes	absent	absent	absent	IP(M)	pattern between C11 and C14
S8	NA(H)	abundant n-alkanes	absent	absent	absent	NA(H)	C13-C16
S9	none	absent	absent	absent	absent	none	plastic pieces
S10	HPD	abundant, Gaussian distribution	present, less abundant than alkanes	present, less abundant than alkanes	present, less abundant than alkanes	HPD	pattern between C10 and C24
S11	OM(M)	absent, peaks seen in profile are not alkanes	absent, peaks seen in profile are not cycloalkanes	present, not recognized pattern	not present in significant amounts	OM(M)	terpenes present between C9 and C12

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S12	AP(L)	absent	absent	present in low levels (C2 alkyl-benzenes)	absent	AP(L)	pattern between C8 and C9
S13	OS(L)	absent	absent	absent	absent	none	no peaks
S14	none	absent, peaks seen in profile are not alkanes	absent, peaks seen in profile are not cycloalkanes	absent, peaks seen in profile are not aromatics	absent	none	cloth pieces

(L)=Light, (M)=Medium, (H)=Heavy, PD=Petroleum Distillate, AP=Aromatic Product, IP=Isoparaffinic Product, NA=Normal-Alkanes Product, NP= Naphthenic-Paraffinic Product, OM= Others-Miscellaneous, OS= Oxygenated Solvent

### Conclusions

This validation demonstrated that:

1. GC-MS #6 has excellent performance for Fire Debris analysis. The obtained results (baseline separation of all peaks, symmetrical peak shape, a range of less than  $\pm 0.02$  minute average retention time for each component with a between-run/within-run of less than 0.3%, a NIST match factor of  $>800$  for all evaluated components) demonstrate the chromatographic parameters tested are appropriate for the analysis. The reproducibility of the instrument was proved to be excellent over weeks due to the E1618 test mixture's components retention times obtained every day of instrument use.
2. In terms of sensitivity, the GC-MS complied with the LOD acceptance criteria by detecting an ignitable liquid concentration of 0.005% v/v, or lower, for all tested classes/sub-classes, except for the Oxygenated Solvents class with a determined LOD of 0.05%. The product used for the test contains light volatile components like ethanol, acetone, and ethyl acetate that can easily evaporate, especially at low concentrations.
3. Carry over was absent in blank (IS) injections after each solution of highest concentration (1% v/v) for LOD determination. Nonetheless, blanks shall be analyzed between samples in real cases all the time as the concentration of any ignitable liquid present is unknown.
4. For selectivity/matrix effects, each ignitable liquid tested was identified in its proper class/sub-class with two analytical techniques - Passive Headspace Concentration (PHSC) with Activated Charcoal Strips (ACS) extracted for 16 hours at 65°C, and Liquid Sample Dilution, using carbon disulfide as the elution/dilution solvent. Although some diesel heavy components were absent (C<sub>18</sub> – C<sub>20+</sub>) with the PHSC technique, it was correctly identified as a Heavy Petroleum Distillate. Using the Solvent Extraction with pentane technique resulted in the missing of light components (as warned by scientific literature) where the oxygenated solvent tested was not detected and the gasoline looks weathered instead of fresh, but presented a diesel chromatogram that looks like neat diesel. No ignitable liquid was detected in negative (matrix only) samples.

5. Flame and miscibility tests performed to liquid samples yielded the expected results. These tests shall be performed to all liquid samples as a “screening” technique. Liquid samples may be diluted between 1 to 0.1%.
6. Although the matrices used contributed extraneous compounds or compounds inherent to ignitable liquids (like terpenes from wood, and aromatics from synthetic material), each ignitable liquid was properly identified from its matrix using the PHSC with ACS technique. This proves selectivity – the ability of the procedure to differentiate unequivocally the analyte in the presence of other components in the sample (although there may be instances when matrix contribution overwhelms a sample with low concentration of IL rendering it undetectable). Notwithstanding, it is highly recommended to submit for analysis comparison samples (whenever possible) along with unknown samples to rule out matrix contribution.
7. Some samples were analyzed using the SIM Fire method after having been analyzed with the Fire method. A comparison between the results of both chromatographic methods showed no significant differences, but the SIM Fire method may still be used on a case by case basis at the discretion of the analyst.
8. In terms of robustness, for PHSC with ACS, keeping the extraction time at 16 hours but changing the extraction temperature resulted in all ignitable liquids identified in their proper class. Light and medium ILs were detected at room temperature, 35°C and 55°C. The diesel pattern obtained at 85°C improved when compared with the one obtained at 65°C (pristine and phytane are clearly visible now). Keeping the extraction temperature at 65°C but changing the extraction time temperature resulted in all ignitable liquids identified in their proper class. Light, medium and heavy ILs were detected after 0.5, 4, 8 and 25 hours of extraction. No ILs were detected in negative (matrix only) samples. To summarize, the result of changing the extraction time and temperature was consistent with effects previously reported in the literature. This step proved the capacity of the method to maintain suitability for intended use by deliberate variations in procedural parameters.
9. Changing the extraction time from about 30 seconds to about 60 seconds to test the robustness of the Solvent Extraction technique resulted in similar results (missing of light components where the oxygenated solvent tested was not detected and the gasoline looks weathered instead of fresh). A neat chromatogram was still obtained for diesel.
10. PHSC with ACS using carbon disulfide shall be the first option for the analysis of solid samples. Solvent Extraction with pentane should be limited to the analysis of small clean solid samples when the analyst suspects a heavy ignitable liquid may be present.
11. Although an extraction at 65°C for 16 hours is considered the “default” test condition, variation in extraction time (from 0.5 to 25 hours) and temperature (from room temperature to 85°C) may be used at the analyst’s discretion depending on how concentrated or diluted any IL present is perceived during the initial evaluation of the submission.
12. Metal cans and nylon arson evidence bags proved to be reliable containers for fire debris evidence.

13. GC-MS #6, the instrumental parameters, and the extraction techniques outlined in this report (with the Solvent Extraction limitations already described) are suitable for Fire Debris Analysis.

### **References**

1. ASTM E1618-14 Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry
2. ASTM E1386-15 Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Solvent Extraction
3. ASTM E1412-16 Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Activated Charcoal
4. ASTM E2549-14 Standard Practice for Validation of Seized-Drug Analytical Methods
5. SWGDRUG Recommendations Part IV B – Quality Assurance/ Validation of Analytical Methods and Supplemental Document SD-2

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