Automated Characterization of Compounds in Fire Debris Samples

Application Note – Forensics | Fire Debris Analysis

Abstract

An automated software package, *Sherlock X*, is presented that characterizes hydrocarbon compounds found in fire debris samples. Using an Agilent 7890 GC with 5977A MSD, this specialized software replaces the manual process of compound naming currently practiced. Automation saves time and generates a more complete, objective analysis of compounds, reducing the chance of bias.

Introduction

Analysis of hydrocarbons in fire debris samples is a critical step in determining the presence or absence of an accelerant, and the type of accelerant used. The chemical extraction procedure is described in Standard Practice ASTM E1412 [1] and yields an extract with hydrocarbons in the C6 to C26 range. Within this extract there are a variety of conformations, including alkanes, cycloalkanes, and aromatics. Because the sample originates from a locale where a fire occurred, a variety of conflating compounds from the background may be present, such as styrenes from carpeting or polyurethane from flooring. The final chromatogram is typically extremely complex, often with more than forty identifiable peaks. (Figure 1.)
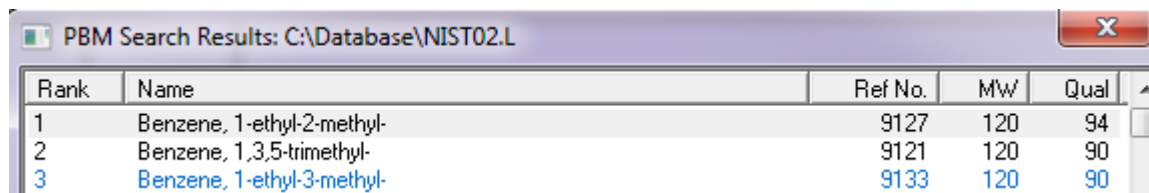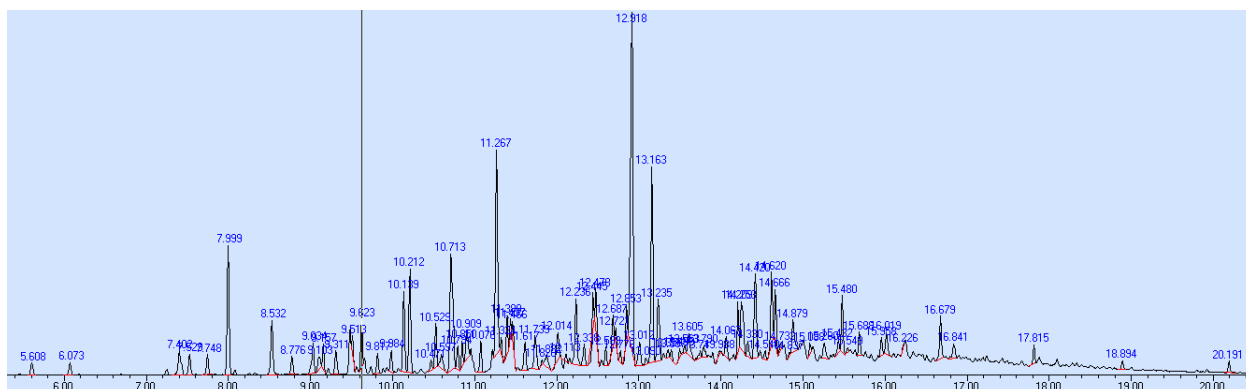

Figure 1. A real-world fire debris chromatogram

The typical approach to analyzing a fire debris chromatogram is for a highly-skilled analyst to evaluate each major peak manually. This evaluation requires considering both the retention time of the peak and also the spectral match against an industry spectral library [2]. Retention time alone is insufficient due to interference from background compounds, while spectral matching rarely gives a unique, well-separated identification, with the correct choice often not being the first one.

Rank	Name	Ref No.	MW	Qual
1	Benzene, 1-ethyl-2-methyl-	9127	120	94
2	Benzene, 1,3,5-trimethyl-	9121	120	90
3	Benzene, 1-ethyl-3-methyl-	9133	120	90

Figure 2. Spectral match showing multiple options.

The experienced analyst develops expected retention times for the compounds of interest from samples of known composition; these retention times are then applied along with the spectral library matches and information about specific ions to manually determine compound naming for chromatographic peaks. Changes to the system, such as installing a new column, will likely require re-assigning these retention times.

Adding more complexity, not all compounds are fully resolved, yielding overlapping peaks that can be difficult to characterize. The peak in Figure 3 has a "shoulder" on the right side, indicating multiple compounds. In this case, the peak is a combination of methylindane (on the left) and tetramethylbenzene (on the right).

The procedure for determining whether an accelerant is present in a sample – and if so what type of accelerant – is detailed in ASTM Standard Procedure E1618 [3]. This procedure requires naming specific sets of compounds. For example, the target compounds for gasoline include three trimethylbenzenes, two tetramethylbenzenes, and a number of methylnaphthalenes, fifteen compounds in all. In addition to naming individual compounds, one must also determine the overall amount of different types of compounds. For gasoline, "the aromatic concentration is generally substantially higher than the alkane concentration." [ibid]

A more efficient and more objective solution to this complex problem is automation. *Sherlock X* is intelligent software that evaluates both retention time and spectral match information to name compounds; it can determine when peaks are impure and separate out the components, and reports not just the individual named compounds but also the total abundance of compound types.

Figure 3. Unresolved peak with shoulder.

Given the individually named compounds, and given the relative abundances of compound types, a technician can quickly and confidently determine the presence or absence of an accelerant.
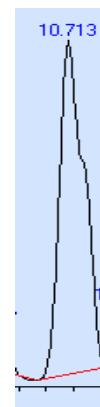
Experimental

Materials

To assure known, expected results, samples of ignitable liquids were obtained from the Ignitable Liquid Reference Collection (ILRC) of the National Center for Forensic Sciences (University of Central Florida, Orlando, Florida) [4]. These materials are provided on coconut charcoal and extracted by adding 1ml carbon disulfide to approximately 5 flakes of charcoal.

Tests were performed using samples of: charcoal lighter fluid (ILRC034); two different diesel fuels (ILRC050 and ILRC364); gasoline at two levels of weathering (ILRC096, 25% weathered, ILRC098, 75% weathered); and kerosene (ILRC374).

To demonstrate peak naming in the presence of background compounds, hundreds of real-world fire debris samples have also been analyzed. These samples were extracted by passive headspace onto activated charcoal strips, following the ASTM E1412 [1].

For each batch of samples, the NIST 2285 Ignitable Liquid Test Mixture was run before any samples. (The ASTM E1618 Test Mix for Fire Debris Analysis may also be used with *Sherlock X*.) Including a calibration mixture in each batch allows *Sherlock X* to adjust the expected peak locations based on known compounds throughout the time range of interest.

Instrumentation and Software

Samples were run on a 7890 GC / 5977A MSD with an Agilent HP5-MS column (30m x 0.25 mm, 0.25 µm). A temperature program starting at 50°C, holding for 3 minutes, ramps to 280°C at 10°C/minute. A final ramp of 60°C/minute to 310°C holding for 3.5 minutes helps remove less volatile compounds.

The MSD was set for full scan mode, from 36 amu to 350 amu. A solvent delay of 2.25 minutes was included so that the MSD would be turned off while the solvent peak eluted.

The Agilent MassHunter software (B.07.03) collected data from the instrument; GCMS ChemStation software (F.01.01) analyzed the data and a specialized ChemStation macro automatically called *Sherlock X* to characterize the compounds.

Results and Discussion

ILRC Samples

Each ILRC sample was processed in four separate batches, with each batch having its own calibration run. Samples were then compared for consistent peak naming, and also to expected results from the ILRC online database.

The example below is ILRC096, Gasoline 25% weathered; the ILRC result is listed and shows four major compounds. (Figure 4.)
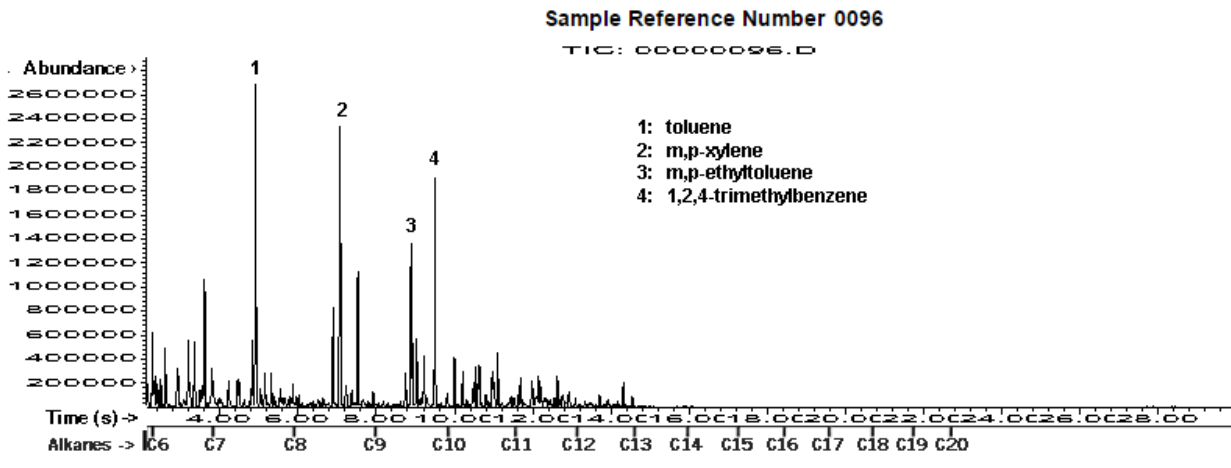

Sample Reference Number 0096
TIC: 00000096.D

1: toluene
2: m,p-xylene
3: m,p-ethyltoluene
4: 1,2,4-trimethylbenzene

Figure 4. Sample 096 from ILRC website

When analyzed by *Sherlock X*, the software reproduced this result with automatic peak naming and chromatographic annotation.

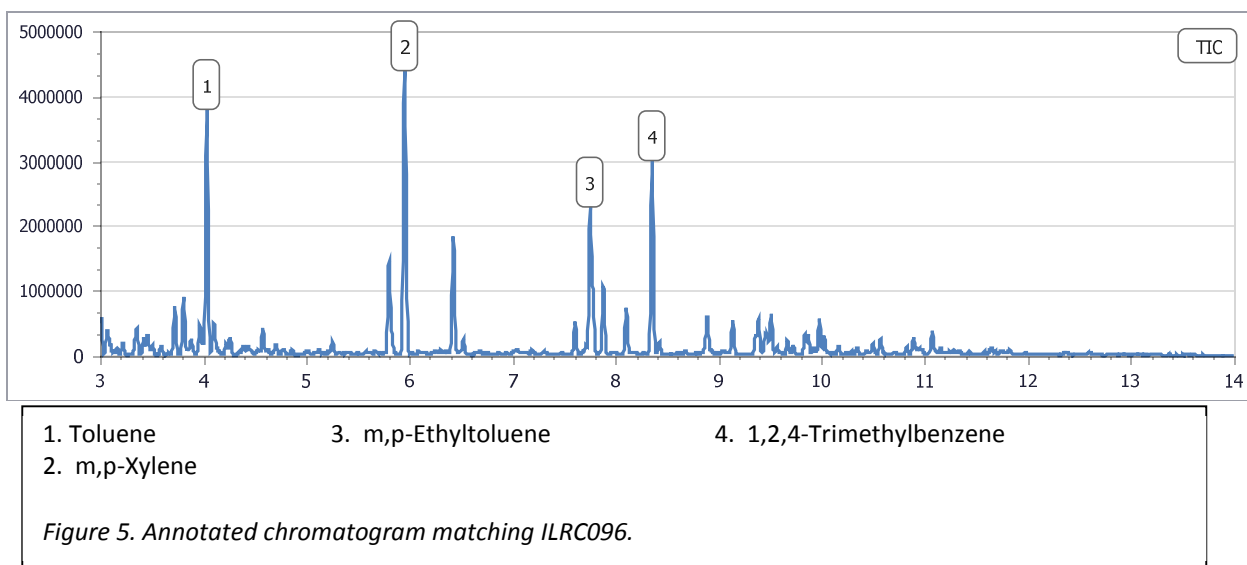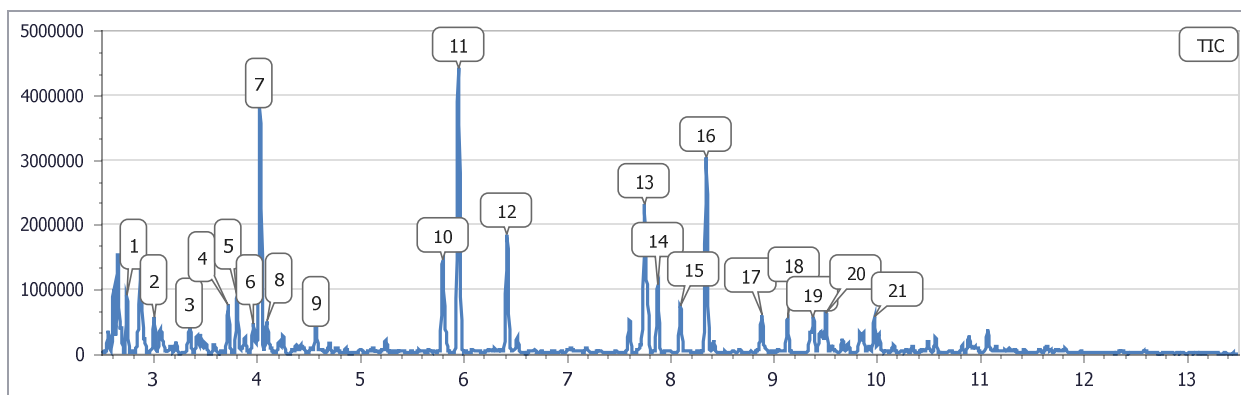1. Toluene   3. m,p-Ethyltoluene   4. 1,2,4-Trimethylbenzene
2. m,p-Xylene

Figure 5. Annotated chromatogram matching ILRC096.

Furthermore, *Sherlock X* identified a total of 21 peaks in this sample with greater than 1% abundance.

1. Methylhexane
2. Heptane
3. Methylcyclohexane
4. 2,3,4-Trimethylpentane
5. 2,3,3-Trimethylpentane
6. 2-Methylheptane
7. Toluene
8. 3-Methylheptane
9. Octane
10. Ethylbenzene
11. m,p-Xylene
12. o-Xylene
13. m,p-Ethyltoluene
14. 1,3,5-Trimethylbenzene
15. o-Ethyltoluene
16. 1,2,4-Trimethylbenzene
17. 1,2,3-Trimethylbenzene
18. Indane
19. m-Propyltoluene
20. p-Ethylxylene
21. 4-Ethyl-o-xylene

*Figure 6. ILRC096 with 21 major compounds automatically identified and annotated.*

Sherlock X generated a report including this image and the full list of compounds with their percentages.

The six different ILRC samples were each run four times, and an average taken to determine the reproducibility of *Sherlock X* results. Table 1 shows a run-to-run deviation of only around 1%, demonstrating the system's reproducibility.

Table 1. Sherlock X Reproducibility		
ILRC#	**Sample Type**	**Deviation from Average**
034	Charcoal Lighter Fluid	0.56%
050	Diesel (Low Sulfur)	0.76%
364	Diesel	0.56%
096	Gasoline (25% Weathered)	0.72%
098	Gasoline (75% Weathered)	0.36%
374	Kerosene	1.23%

Two gasoline samples were included in this sample set, one 25% weathered, the other 75% weathered. Comparing the 75% weathered gasoline to 25% weathered, one finds that the more volatile compounds such as heptane, methylcyclohexane and toluene were either significantly decreased or disappeared altogether, while less volatile compounds such as methylindanes and naphthalene were increased, as expected [5].

The two diesels were different brands, one of which is low sulphur, and show a difference of approximately 5%. (By comparison, the diesel and charcoal lighter fluid differ by 33%.) Both are clearly heavy petroleum distillates, showing the telltale alkane series in the chromatogram (Figure 7). *Sherlock X* names twenty smaller compounds not shown, the annotations simplified for readability.
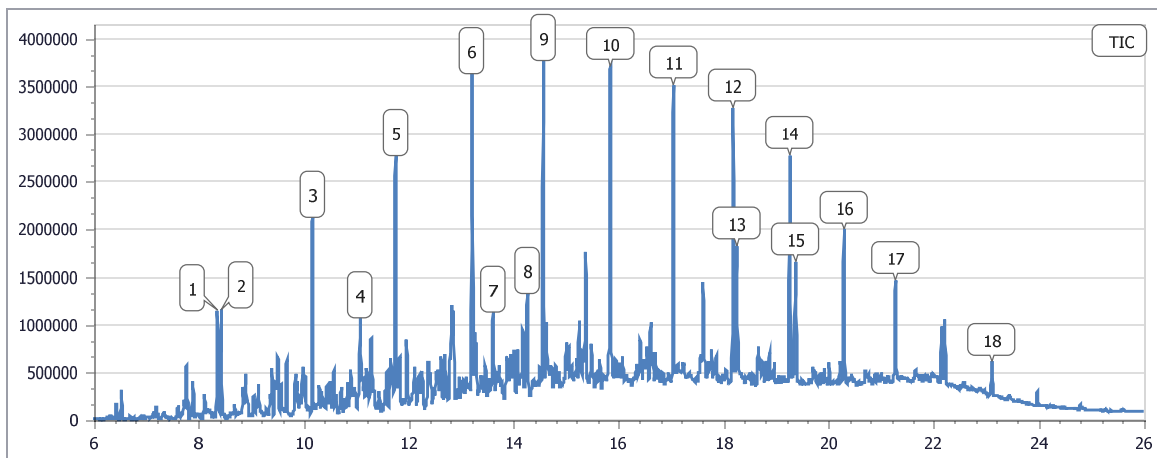
1. 1,2,4-Trimethylbenzene	7. 2,7-Dimethyltetralin	13. Pristane
2. Decane	8. Trimethyldodecane	14. Octadecane
3. Undecane	9. Tetradecane	15. Phytane
4. 5-Methylindan	10. Pentadecane	16. Nonadecane
5. Dodecane	11. Hexadecane	17. Eicosane
6. Tridecane	12. Heptadecane	18. Docosane

Figure 7. Diesel sample highlighting the alkane series.

Category Analysis

Sherlock X can categorize the compounds identified in a sample into user-defined groups. These groups can be defined to match those found in the ASTM E1618, such as aromatics and alkanes. Table 2 shows the categorized results for each of the different ILRC samples run.

Table 2. Cross-tabulation of compound types by sample		Aromatics	Cycloalkanes	Condensed Rings	Alkanes-straight	Alkanes-branched
ILRC#	Sample Type					
034	Charcoal Lighter Fluid		19.39	1.23	45.31	34.07
050	Diesel (Low Sulfur)	14.20		12.22	58.52	14.20
364	Diesel	9.12		8.44	68.17	13.65
096	Gasoline (25% Weathered)	74.65	3.03	3.96	3.98	14.38

098	Gasoline (75% Weathered)	79.95		12.30	3.75	3.04
374	Kerosene	11.68	5.22	6.68	55.34	20.84

In this table, one can quickly see the closeness in composition between the two diesel fuels, as well as the relative closeness between the two weathered gasoline samples.

Real-world Samples

Sherlock X has been used to analyze hundreds of real-world samples. An example of the result for a positive sample is shown in Figure 8. In this case annotations have been included demonstrating the broad range of compounds identified by Sherlock X.
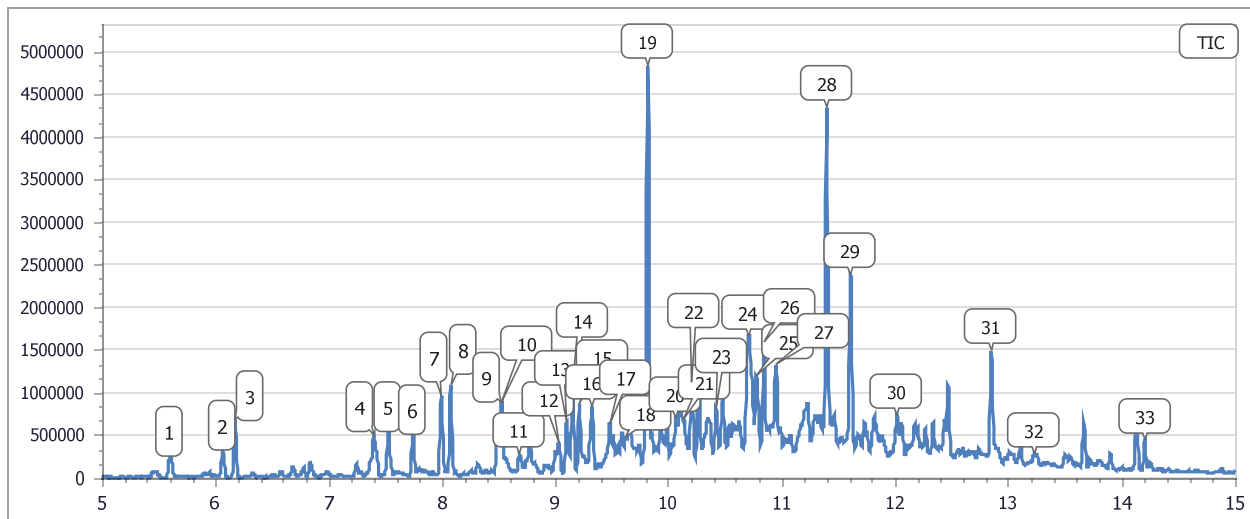
1. m,p-Xylene	12. m-Propyltoluene	23. Pentylcyclohexane
2. o-Xylene	13. 5-Methyldecane	24. 5-Methylindan
3. Nonane	14. p-Ethylxylene	25. 4-Methylundecane
4. m,p-Ethyltoluene	15. 2-Methyldecane	26. 2-Methylundecane
5. 1,3,5-Trimethylbenzene	16. 3-Methyldecane	27. 3-Methylundecane
6. o-Ethyltoluene	17. 4-Ethyl-m-xylene	28. Dodecane
7. 1,2,4-Trimethylbenzene	18. 4-Ethyl-o-xylene	29. Dimethylundecane
8. Decane	19. Undecane	30. Hexylcyclohexane
9. Cymene	20. 2-Methyldecalin	31. Tridecane
10. 1,2,3-Trimethylbenzene	21. 1,2,4,5-Tetramethylbenzene	32. 1,4-Dimethyltetralin
11. Butylcyclohexane	22. 1,2,3,5-Tetramethylbenzene	33. Tetradecane

Figure 8. Real-world sample with identified background compounds.

Annotated as 9 and 10, cymene and 1,2,3-trimethylbenzene are overlapping peaks that Sherlock X has been able to deconvolve. (Figure 9.)

Sherlock X identifies a number of compounds that may indicate pyrolysis of background materials such as carpet. The sample in Figure 10 has hydrocarbons which likely come from flooring.
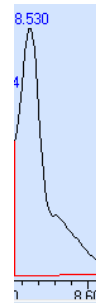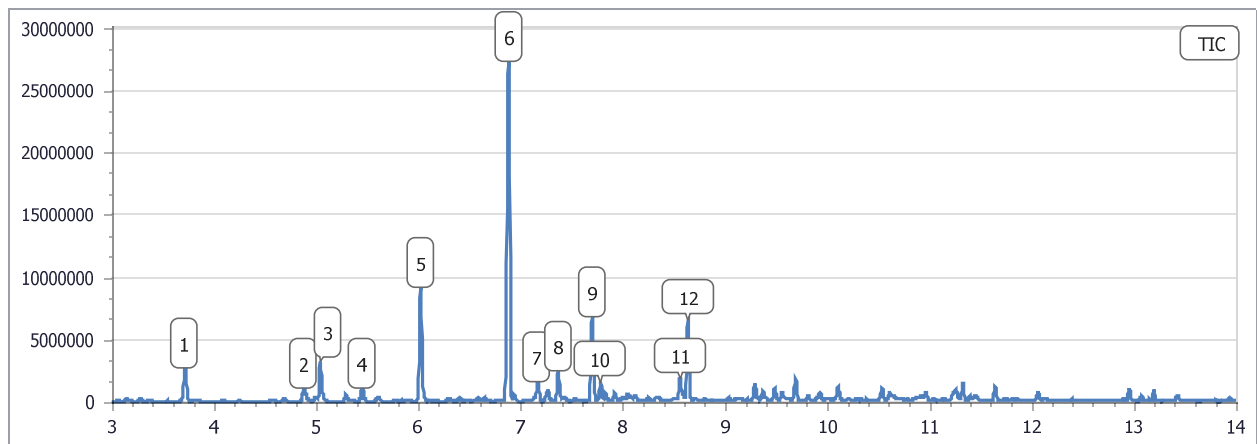

Figure 9. Overlapping Peak

Figure 10. Real-world negative sample with identified background compounds.

1. Toluene
2. Furfural
3. Dimethylheptene
4. Ethylbenzene
5. Styrene
6. a-Pinene
7. Camphene
8. Benzaldehyde
9. b-Pinene
10. Methylstyrene
11. Cymene
12. Limonene

Conclusion

Using *Sherlock X* to characterize compounds in a fire debris sample yields many benefits:

- Saving the technician the time and tedium of manual analysis (~30 minutes/sample)
- Yielding a more complete result with many more compounds named than would be done manually
- Developing an unbiased, objective standard for compound naming
- Creating categorized results automatically
- Generating visually appealing, easily understood reports with annotated chromatograms

References

1. ASTM E1412 – 12 (2012), Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration With Activated Charcoal.
2. P. Koussiates, *Fire and Arson Investigator*, **66**, 30-40.
3. ASTM E1618 – 14 (2014), Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry.
4. Ignitable Liquids Reference Collection website, ilrc.ucf.edu.
5. J. Hendriske, M. Grutters and F. Shaefer, *Identifying Ignitable Liquids in Fire Debris*, Academic Press, 2015, 43-44.

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