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.

![Spectral match showing multiple options.](image)

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.

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.)

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

Figure 4. Sample 096 from ILRC website

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

Figure 5. Annotated chromatogram matching ILRC096.
Furthermore, *Sherlock X* identified a total of 21 peaks in this sample with greater than 1% abundance.

![Image](image-url)

*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>
<thead>
<tr>
<th>ILRC#</th>
<th>Sample Type</th>
<th>Deviation from Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>034</td>
<td>Charcoal Lighter Fluid</td>
<td>0.56%</td>
</tr>
<tr>
<td>050</td>
<td>Diesel (Low Sulfur)</td>
<td>0.76%</td>
</tr>
<tr>
<td>364</td>
<td>Diesel</td>
<td>0.56%</td>
</tr>
<tr>
<td>096</td>
<td>Gasoline (25% Weathered)</td>
<td>0.72%</td>
</tr>
<tr>
<td>098</td>
<td>Gasoline (75% Weathered)</td>
<td>0.36%</td>
</tr>
<tr>
<td>374</td>
<td>Kerosene</td>
<td>1.23%</td>
</tr>
</tbody>
</table>

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, methylcylohexane 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.

![Chromatogram](image)

*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>
<thead>
<tr>
<th>ILRC#</th>
<th>Sample Type</th>
<th>Aromatics</th>
<th>Cycloalkanes</th>
<th>Condensed Rings</th>
<th>Alkanes-straight</th>
<th>Alkanes-branched</th>
</tr>
</thead>
<tbody>
<tr>
<td>034</td>
<td>Charcoal Lighter Fluid</td>
<td>19.39</td>
<td>1.23</td>
<td>45.31</td>
<td>34.07</td>
<td></td>
</tr>
<tr>
<td>050</td>
<td>Diesel (Low Sulfur)</td>
<td>14.20</td>
<td>12.22</td>
<td>58.52</td>
<td>14.20</td>
<td></td>
</tr>
<tr>
<td>364</td>
<td>Diesel</td>
<td>9.12</td>
<td>8.44</td>
<td>68.17</td>
<td>13.65</td>
<td></td>
</tr>
<tr>
<td>096</td>
<td>Gasoline (25% Weathered)</td>
<td>74.65</td>
<td>3.03</td>
<td>3.96</td>
<td>3.98</td>
<td>14.38</td>
</tr>
</tbody>
</table>
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.
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](image)

![Figure 10. Real-world negative sample with identified background compounds.](image)

| 1. Toluene | 5. Styrene | 9. b-Pinene |
| 2. Furfural | 6. a-Pinene | 10. Methylstyrene |
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