Final Report

1. Title of Project — *Fast Gas Chromatography Capabilities in Arson Debris Analysis*

2. Principle Investigator

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3. Report ID and Period — Final Report (April 6, 2007 – November 30, 2007)

4. Abstract

This project assesses the merits of Fast Gas Chromatography (Fast GC) in the determination of ignitable liquids in a variety of matrices. *Forensic Sciences: Review of Status and Needs* clearly elucidates the need for further advances in this field; and current analytical literature points to Fast GC as a separation technique capable of just such advances. Data from this study illustrate that Fast GC alone reduces chromatographic retention times by 60% in the analysis of ignitable liquids. The study also demonstrates that the gains in resolution by switching from helium to hydrogen as a carrier gas (mobile phase) far exceed the resolution losses from the shorter Fast GC minibore column. The combination of these approaches (Fast GC and hydrogen carrier gas) produces phenomenal improvements in the analysis of ignitable liquids as the 60% reduction in retention times is accompanied by increases in resolution of up to 500%. These improvements in separation by Fast GC (hydrogen) compared with conventional GC (helium) are consistently observed in a vast variety of ignitable liquid analyses as well as the analysis of ignitable liquids recovered from controlled burn matrices such as asphalt shingles, carpet, carpet padding, and softwood lumber. The practical significance of this work for crime laboratories is two-fold with the potential increase in sample throughput and an improved detection of potential ignitable liquids through better resolution. There is, however, a need for serious safety protocols if hydrogen is used as a carrier gas in a gas chromatography – mass spectrometer system rather than the GC-FID system used in this study.

5. Project Description

While autosamplers have increased sample throughput in trace units across the nation's crime laboratories, many labs still find themselves desiring higher sample throughput, especially in the area of chromatography. From an instrumental perspective, the stable, rapid heating cycles of Fast GC coupled with narrower capillary columns and high phase ratio result in more theoretical plates per meter, and this increase enables fast separations with potentially superior resolution compared to conventional GC if hydrogen replaces helium as the carrier gas.

Switching to Fast GC from a conventional unit is a relatively simple, inexpensive proposition. For example, an Agilent 6890 GC adaptation to Fast GC involves upgrading the power source to either a 220 V or 240 V (preferred) service, installation of a high-heat oven shroud, power cord, and narrower capillary column. Using hydrogen as a carrier gas in Fast GC

results in further increases in species resolution. The instrumentation upgrade may cost as little as $1,000-$2,000.

This project is designed to test the hypothesis that Fast GC is a beneficial technique in the area of ignitable liquids analysis. The experimental design uses both solid phase microextraction (SPME) and traditional activated charcoal (ACS) strip to pre-concentrate single compound ignitable liquids (i.e. toluene) and common ignitable liquids with multiple compounds (i.e. gasoline). These volatiles are analyzed by conventional GC (helium mobile phase) and Fast GC (hydrogen mobile phase), and the results are statistically compared to test the hypothesis that Fast GC with hydrogen mobile phase provides much faster separation and higher resolution than conventional GC.

6. Project Objectives

The goal of this research project is to bridge the gap between the current status of techniques used in the analysis of arson residues and the need of the forensic community for method development for recovery of ignitable liquid residues from a variety of matrices as described in *Forensic Sciences: Review of Status and Needs*. The primary objective of this project is to provide and disseminate an enhanced understanding of Fast GC and its potential benefits (resolution, effectiveness, and throughput) to the detection of ignitable liquid residues in arson debris. General analytical literature suggests enormous gains in sample throughput are possible through Fast GC separation. If this assessment confirms this potential impact, many GCs currently used in crime laboratories could be easily adapted to Fast GC for $1,000 - $2,000 in additional equipment cost providing 220 or 240 V service is available.

7. Procedures

Materials and Equipment

This project utilizes both activated charcoal strip (ACS) and solid phase microextraction (SPME) pre-concentration methods. Standard series of "weathered" (5% - 95%) ignitable liquids including gasoline, petroleum distillates, isopars, norpars, and other miscellaneous solvents are prepared by evaporating each parent solution under high-purity nitrogen. ASTM standards are purchased from suppliers such as Fisher Scientific and Sigma Aldrich, and common accelerants such as gasoline and petroleum distillates are purchased from local suppliers.

The primary instrumentation for the project includes three GC units. The UWP Chemistry Program recently (2006) acquired an Agilent 6890 Fast GC-FID/ECD through the University of Wisconsin System *Laboratory Modernization* program. Standards and samples are analyzed using this Fast GC at UWP, a Shimadzu17A-QP5050a GC-MS at UWP, and an Agilent 6890-6972 GC-MS at Wisconsin State Crime Laboratory – Madison (WSCL-M) with optimized conditions for each instrument.

Experimental

Characterization of the accelerants by each GC method follows the current WSCL-M protocol for analysis of arson debris. A 10.0 µL sample of an accelerant is pipetted onto a small piece of Kimwipe paper and placed inside an unused paint can in methodology similar to that

used in the WSCL-M ACS method. The sample is heated to 70ºC. From this point pre-concentration by ACS follows the WSCL-M protocol with regards to analyte loading on the strip and solvent wash leading to GC injection. Pre-concentration by SPME involves 30-60 minute headspace adsorption (depending upon the degree of saturation of the 100-µm PDMS fiber) and 1.0 minute analyte desorption in the GC inlet. A *Merlin* microseal inlet septum minimizes septa coring from the SPME apparatus. Samples analyzed by conventional GC follow instrumental parameters outlined in the WSCL-M protocol. The instrumental parameters for the Fast GC analysis are first determined from theoretical calculations, literature results in associated fields, and empirical work and refined experimental to an optimum separation. ASTM standards and other certified references materials (i.e. GRO mixed standard) are used to confirm retention times and as check standards as needed.

The primary identifying constituents of each accelerant are used to assess the reduction in retention time by Fast GC separation. Retention times are compared for Fast GC and conventional GC using a one-way analysis of variance ($p < 0.05$). Resolutions calculated by the instrumentation software are used to compare the pre-concentration techniques (SPME and ACS) as well as the separation performance of the Fast and conventional GC methods. If no statistical difference in retention time is noted in this comparison or another factor does not limit its application, SPME is used to pre-concentrate the remaining samples and standards to increase sample throughput and sensitivity. The superior sensitivity, in theory, would provide a more challenging separation for each separation technique.

If Fast GC represents a significant time savings in analysis of accelerant standards, the second phase of the project will examine accelerants in complex matrices mimicking those in actual arson cases. Matrices such as asphalt, carpet, upholstery fabrics, dry-wall, framing materials, carpet, and carpet padding will be spiked with 0.5 to 10 µL of an accelerant and analyzed by conventional and Fast GC with the sample treatment procedures outlined earlier in this section. Statistical assessment following that outlined earlier will be applied to these samples to compare the separation techniques.

8. Results/Discussion

There are several significant findings in this study. There is no significant difference in these results with respect to pre-concentration platform (SPME and ACS); however, as literature and previous work would suggest, the SPME pre-concentration technique, 100 µm PDMS coating, is more capable in extracting low-level polyaromatic hydrocarbons. The results clearly demonstrate a significant reduction in gas chromatography retention times across the board for all ignitable liquids using the shorter capillary column and heating parameters of Fast GC (Figures 1-5, Table1). This result agrees with the previously published body of general work supporting faster analyses using this technique.

A primary concern with the Fast GC technique is a loss of resolution. This is observed when comparing the Fast GC and conventional GC while both are employing the same carrier gas. The substitution of hydrogen from the helium carrier gas (mobile phase) off-sets this loss of resolution with the shorter Fast GC minibore column. Experimental data from this project demonstrates that the switch to hydrogen from helium carrier gas has a significantly positive effect on resolution.

While either of these findings have a potential benefit in the analysis of ignitable liquids recovered from arson debris, by combining the two ideas (Fast GC and hydrogen carrier gas) the

results are dramatic (Figures 1-5). Using resolution and retention times as focal figures of merit, the trend of increased performance is further enhanced. The components of ignitable liquids such as gasoline, petroleum distillates, and isopars are separated with higher resolution (up to 500% increase) in much shorter analysis times (as little as 36% original run time). The typical improvement is exemplified by the separation of 95% evaporated gasoline. Table 1 demonstrates the dramatic decreases in retention times for the separation, and Table 2 shows the outstanding improvements in resolution. Similar results are observed with each multi-component ignitable liquid analyzed and noted in Table 3.

These increases in resolution play a significant role in enabling a rapid separation of these ignitable liquids even when they are extracted from a variety of complex arson debris matrices such as carpet, carpet padding, softwood framing materials, and asphalt shingles. Figure 5 illustrates the comparison of conventional (helium carrier) and Fast GC (hydrogen carrier) for such a matrix. Data from the other ignitable liquids analyzed demonstrates a similar trend.

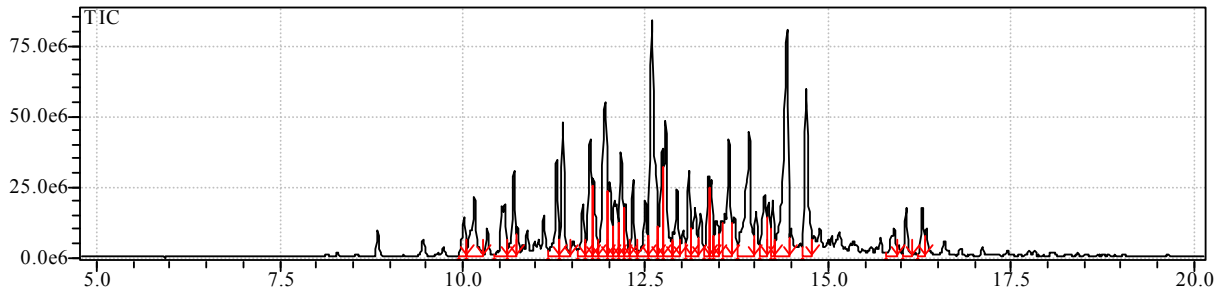
Given the body of data, Fast GC with hydrogen carrier gas provides superior resolution and faster analysis times compared with conventional GC with helium as the mobile phase. While the potential for increased sample throughput and/or increased capability of identifying an ignitable liquid from debris is significant, these experiments with the hydrogen carrier gas used a flame ionization detector (FID) with the Fast GC rather than a mass spectrometer (MS). Compressibility and safety factors must be addressed for MS detectors and extra precautions taken when using hydrogen with MS rather than FID detectors.

9. Dissemination Discussion

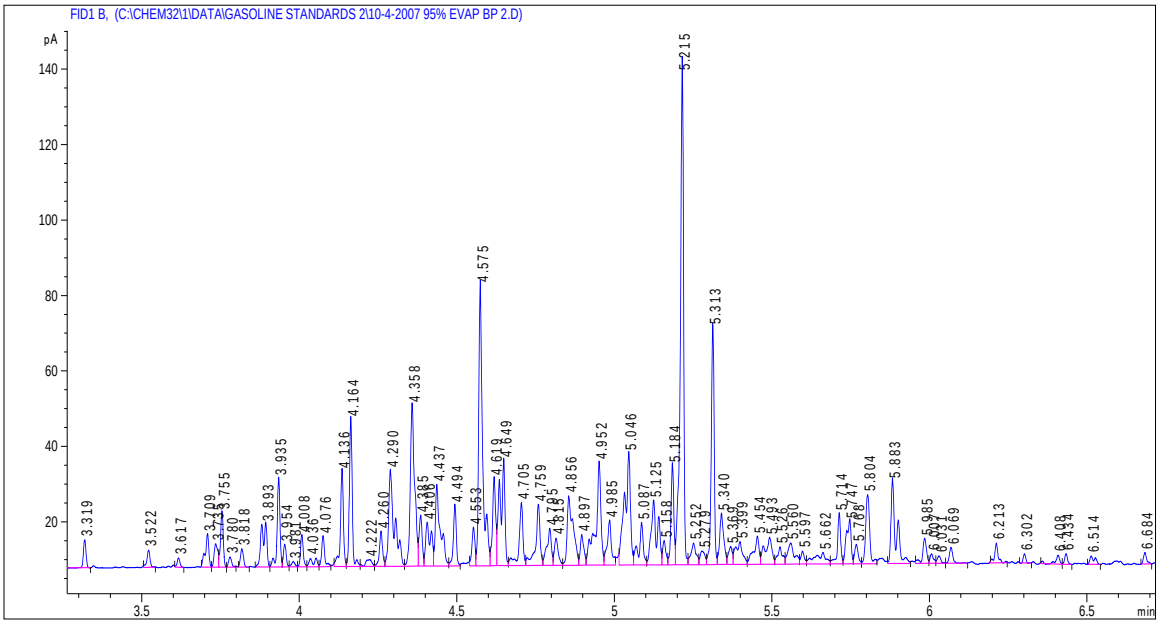
This work was presented in the poster session of the Midwest Association of Forensic Scientists 2007 annual meeting in Traverse City, MI. Further dissemination is planned in the form of poster presentation in the American Academy of Forensic Sciences annual meeting in Washington, DC (February 2008). This work and subsequent findings will also be presented at the 2009 Pittsburgh Conference through UW-Platteville and personal travel support. If there is enough interest, I am also open to leading a discussion group or workshop at MAFS 2008. Dissemination will also include submitting a paper to the *Journal of Forensic Science* during summer 2008.

10. Discussion of Problems that Have Arisen

The sole problem that arose was the late withdrawal of a student who was committed to work on the project full-time during the summer 2007 session. While several students were hired to work part-time during the last six weeks of the project, the funds tasked for student wages were not completely spent. Approximately $2,000 of appropriated funding was not spent with approximately $1000 attributed to unspent travel funds, and the remainder to unspent student wage and fringe. If some means for spending this money through an extension is possible, the project would benefit specifically through an increased dissemination as the travel money would be used to fund dissemination at the 2008 American Academy of Forensic Science meeting.

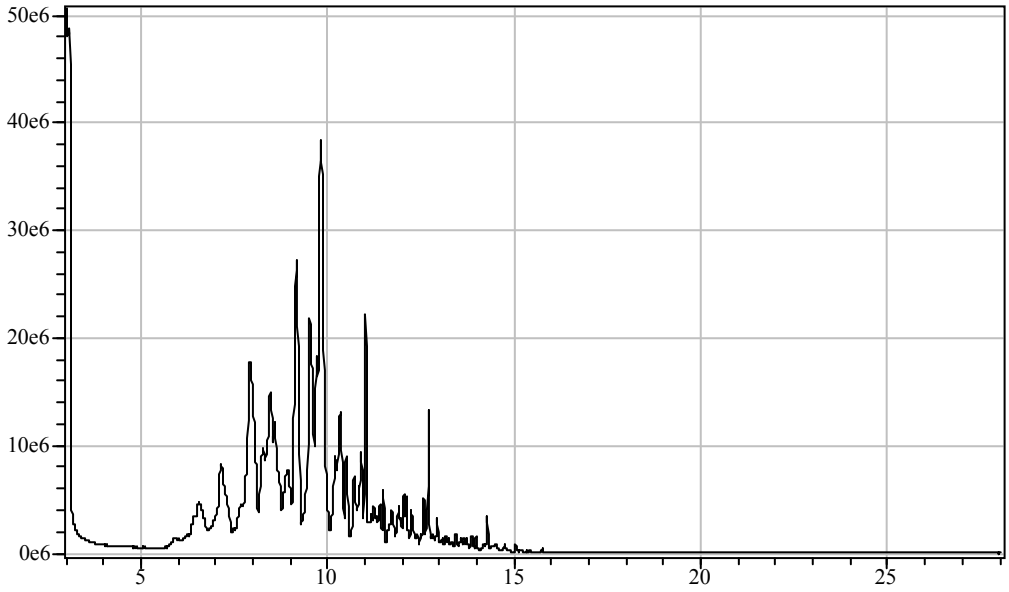


(Conventional GC)

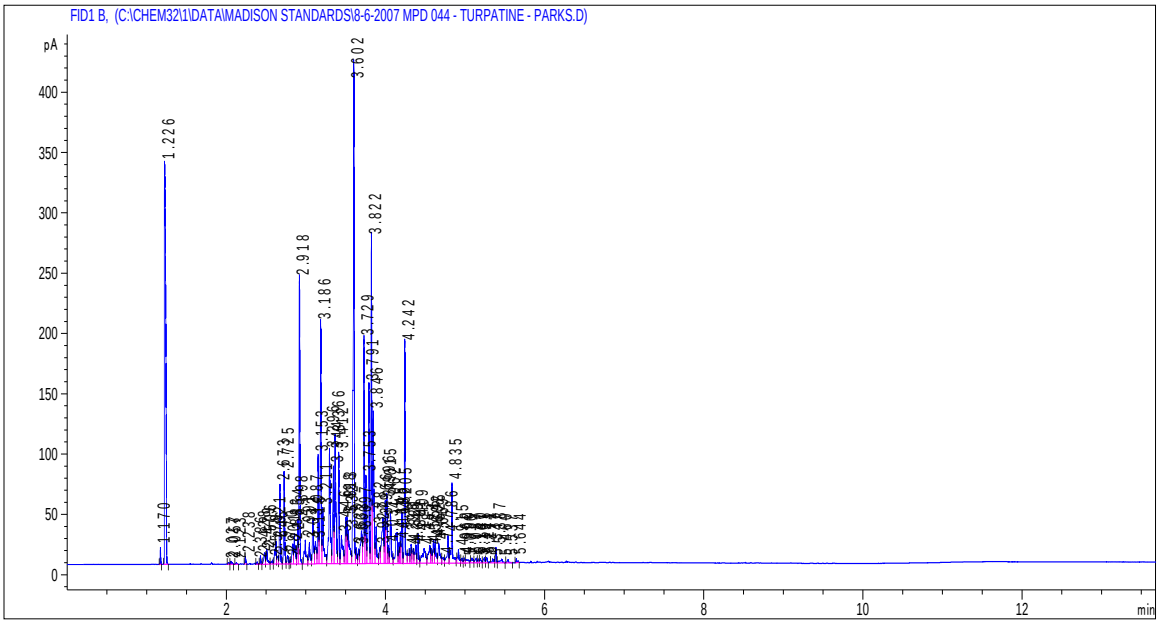


(Fast GC)

Figure 1. A Comparison of Fast GC (Hydrogen Carrier Gas) and Conventional GC (Helium Carrier Gas) Separations of 95% Evaporated Gasoline

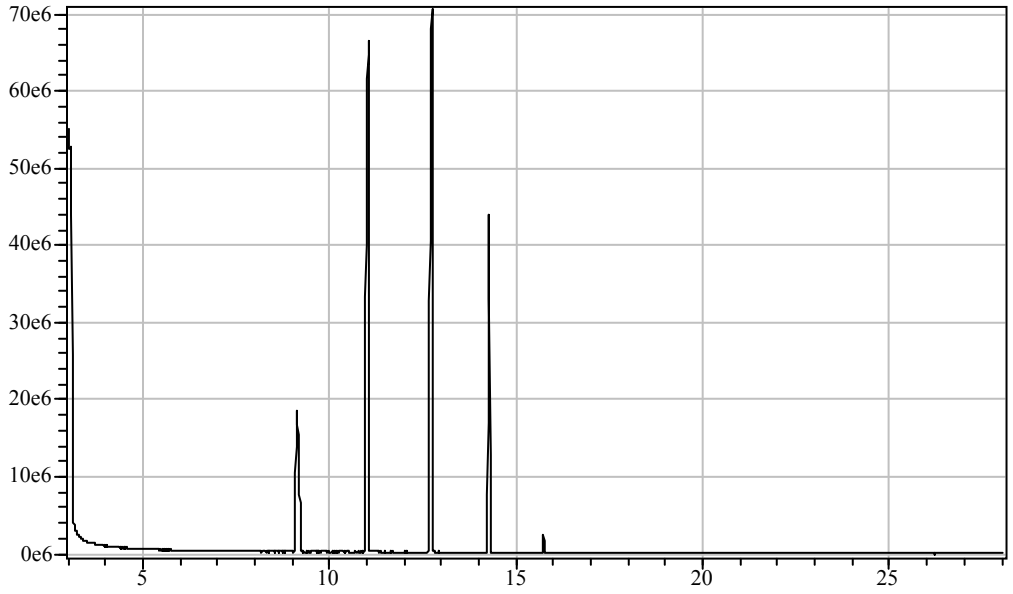


(Conventional GC)

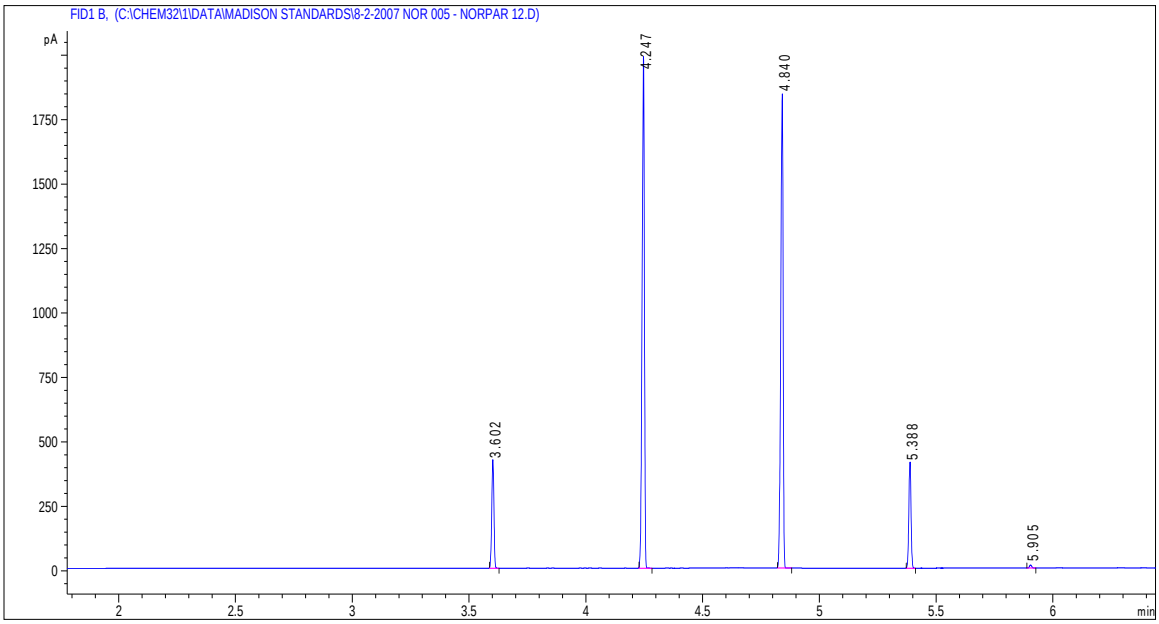


Fast GC

Figure 2. A Comparison of Fast GC (Hydrogen Carrier Gas) and Conventional GC (Helium Carrier Gas) Separations of a Medium Petroleum Distillate

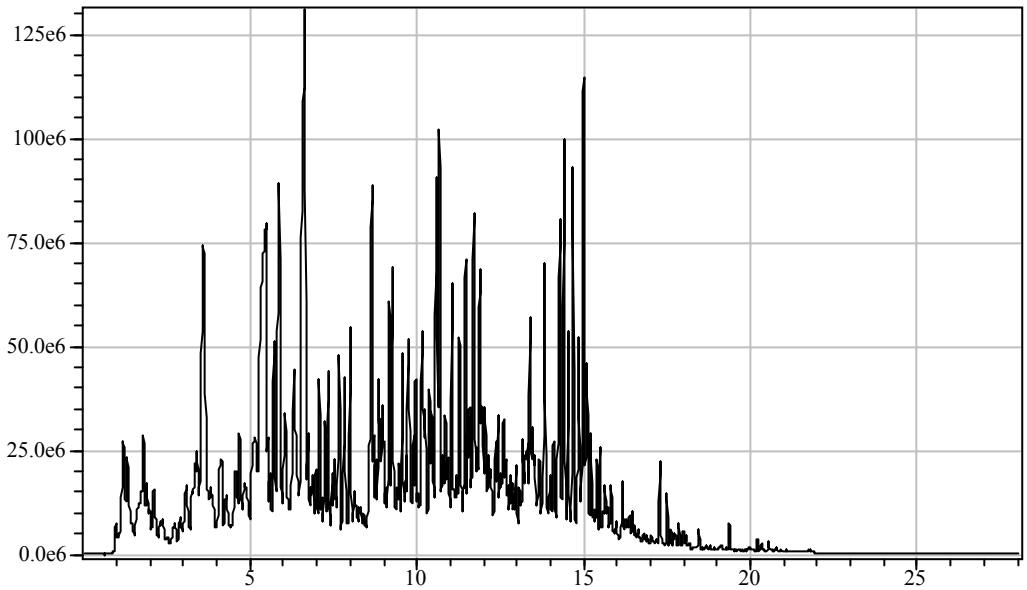


Conventional GC

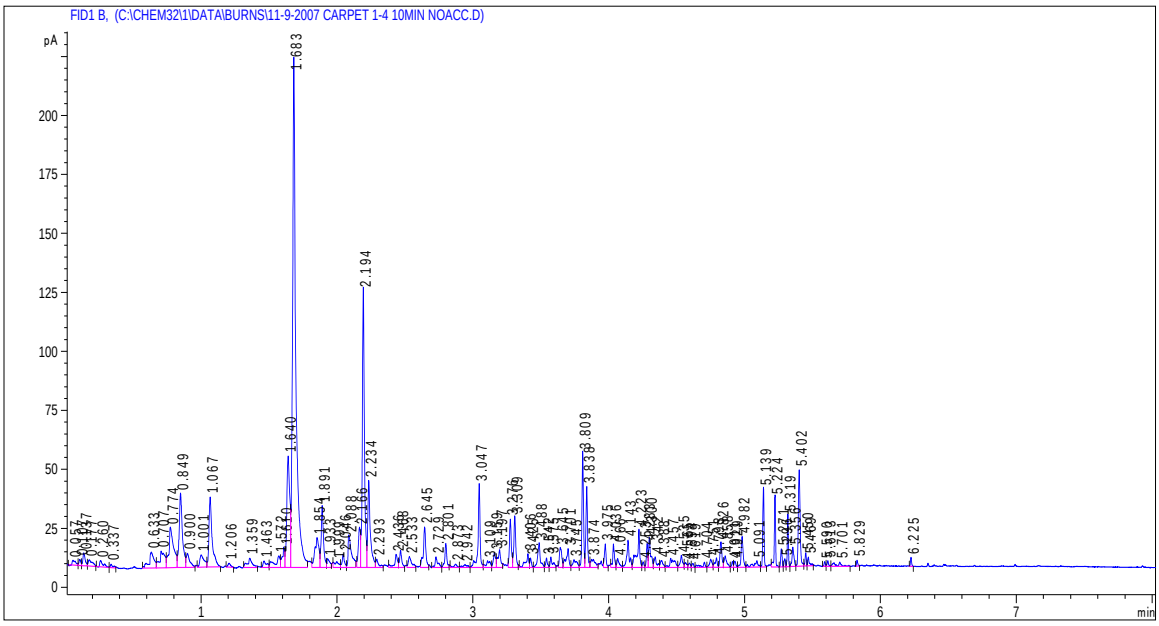


Fast GC

Figure 3. A Comparison of Fast GC (Hydrogen Carrier Gas) and Conventional GC (Helium Carrier Gas) Separations of Norpar "12"

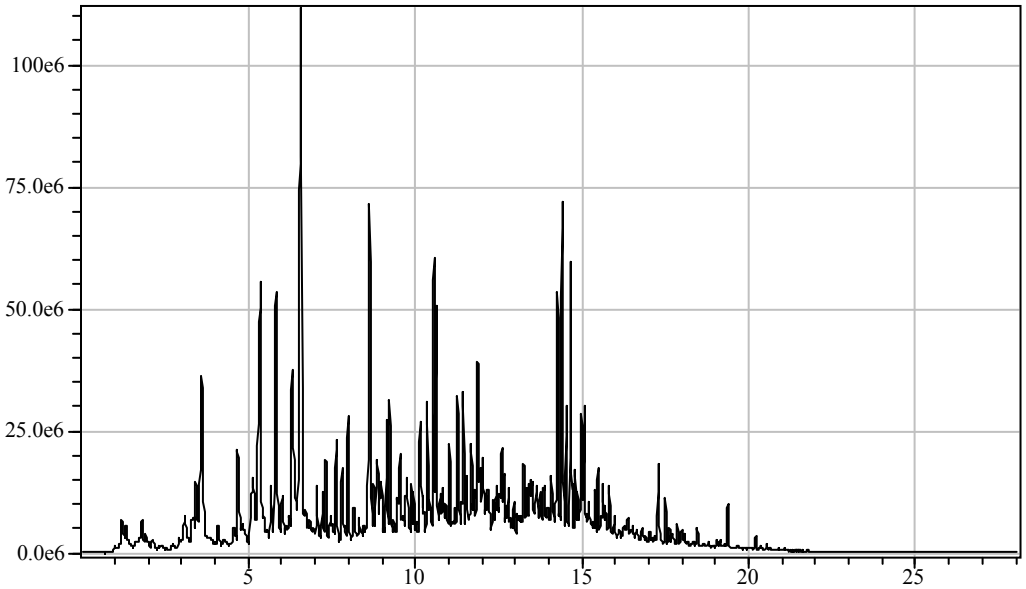


Conventional GC

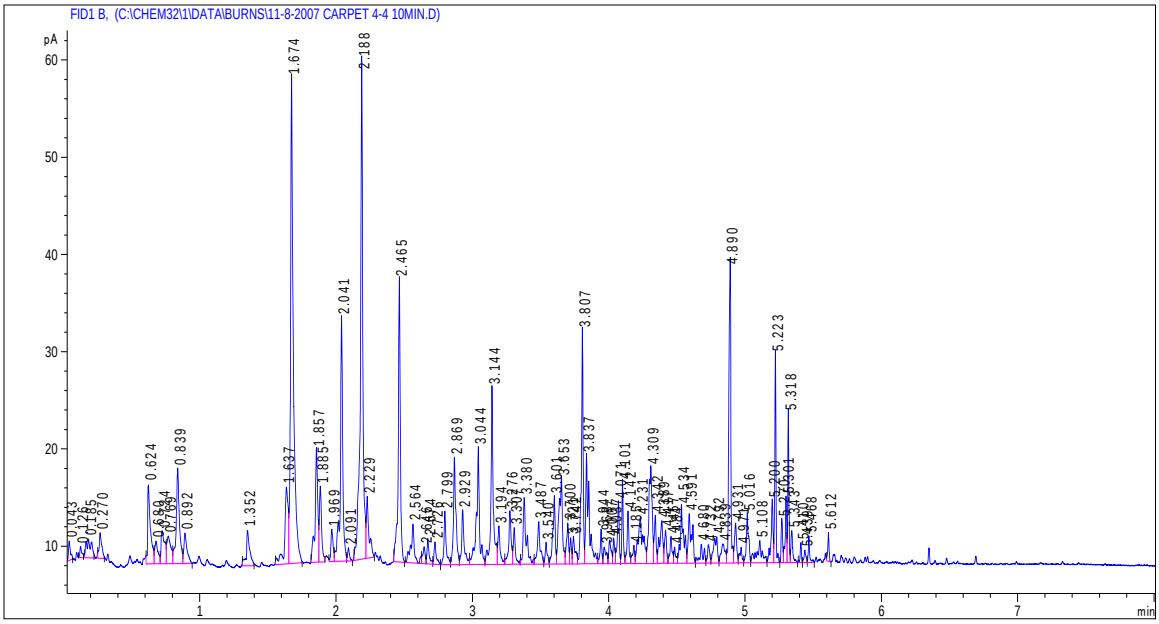


Fast GC

Figure 4. A Comparison of Fast GC (Hydrogen Carrier Gas) and Conventional GC (Helium Carrier Gas) Separations of Unspiked Carpet Burned Ten Minutes



Conventional GC



Fast GC

Figure 5. A Comparison of Fast GC (Hydrogen Carrier Gas) and Conventional GC (Helium Carrier Gas) Separations of Carpet Spiked with 500.0 µL Gasoline and Burned Ten Minutes

Table 1. A Statistical Comparison* of Fast GC and Conventional GC Retention Times for the Separation of 95% Evaporated Gasoline (Bolded Values Indicate Statistical Significance)

Compound Class	Retention Time (min) (Fast GC)	Retention Time (min) (Conventional)
C4-alkylbenzene	3.93#	10.69#
C4-alkylbenzene	4.14	11.28
C4-alkylbenzene	4.16	11.37
C5-alkylbenzene	4.29	11.74
C5-alkylbenzene	4.36	11.95
C5-alkylbenzene	4.44	12.16
C5-alkylbenzene	4.49	12.32
naphthalene	4.57	12.58
C5-alkylbenzene	4.65	12.77
C5-alkylbenzene	4.70	12.93
C5-alkylbenzene	4.76	13.09
C5-alkylbenzene	4.86	13.39
C1-naphthalene (2-methylnaphthalene)	4.95	13.64
C1-naphthalene (1-methylnaphthalene)	5.04	13.91
C2-naphthalene	5.21	14.43
C2-naphthalene	5.31	14.70

All standard deviations $\leq \pm 0.02$ min

* All differences in retention times observed are highly statistically significant ($p < 1 \times 10^{-6}$)

Table 2. A Statistical Comparison of Fast GC and Conventional GC Resolution for the Separation of 95% Evaporated Gasoline (Bolded Values Indicate Statistical Significance)

Compound Class	Resolution (Fast GC)	Resolution (Conventional)	α-value
C4-alkylbenzene	1.30 ± 0.05	0.934 ± 0.011	**2×10^{-19}**
C4-alkylbenzene	3.78 ± 0.04	3 ± 2	0.5#
C4-alkylbenzene	1.77 ± 0.03	1 ± 2	0.7#
C5-alkylbenzene	1.07 ± 0.01	0.91 ± 0.10	**0.003**
C5-alkylbenzene	2.16 ± 0.06	0.6 ± 0.7	**0.0004**
C5-alkylbenzene	1.01 ± 0.08	0.4 ± 0.2	**1×10^{-5}**
C5-alkylbenzene	2.7 ± 0.8	0.5 ± 0.8	**0.0001**
naphthalene	1.19 ± 0.02	0.786 ± 0.015	**6×10^{-16}**
C5-alkylbenzene	2.2 ± 0.5	1.5 ± 0.5	0.04
C5-alkylbenzene	2.92 ± 0.03	1.60 ± 0.13	**2×10^{-11}**
C5-alkylbenzene	2.70 ± 0.04	1.08 ± 0.16	**7×10^{-7}**
C5-alkylbenzene	2.07 ± 0.02	1.4 ± 1.2	0.21#
C1-naphthalene	1.88 ± 0.03	1.6 ± 0.3	0.06
C1-naphthalene	2.26 ± 0.07	1.42 ± 0.04	**1×10^{-12}**
C2-naphthalene	1.72 ± 0.07	1.3 ± 0.3	**0.006**
C2-naphthalene	2.8 ± 0.6	2.2 ± 0.3	**0.03**

Likely a result of the large variance in the Conventional Resolution data

Table 3. Ignitable Liquids Analyzed in this Comparison Study of Fast and Conventional GC

98% evaporated gasoline
95% evaporated gasoline
90% evaporated gasoline
75% evaporated gasoline
50% evaporated gasoline
25% evaporated gasoline
10% evaporated gasoline
95% evaporated E-85 gasoline
90% evaporated E-85 gasoline
75% evaporated E-85 gasoline
50% evaporated E-85 gasoline
25% evaporated E-85 gasoline
10% evaporated E-85 gasoline
LPD2 – camp fuel
LPD3 – lighter fluid
LPD4 – brush cleaner
LPD8 – handwarmer fluid
LPD15 – stove fuel
MPD1 – charcoal starter
MPD24 – furniture cleaner
MPD29 – odorless charcoal starter fluid
MPD44 – turpatine
HPD14 – liquid wrench
HPD8 – diesel
HPD11 – diesel #2 (neat)
98% evaporated diesel #2
75% evaporated diesel #2
50% evaporated diesel #2
lamp oil "A"
98% evaporated lamp oil "A"
75% evaporated lamp oil "A"
50% evaporated lamp oil "A"
lamp oil "B"
98% evaporated lamp oil "B"
75% evaporated lamp oil "B"
50% evaporated lamp oil "B"
kerosene "A" (neat)
98% evaporated kerosene "A"
75% evaporated kerosene "A"
50% evaporated kerosene "A"
kerosene "B" (neat)
98% evaporated kerosene "B"
75% evaporated kerosene "B"
50% evaporated kerosene "B"
No. 2 fuel oil (neat)
90% evaporate No. 2 fuel oil
75% evaporate No. 2 fuel oil
50% evaporate No. 2 fuel oil
25% evaporate No. 2 fuel oil
camp fuel (neat)
98% evaporated camp fuel
75% evaporated camp fuel
50% evaporated camp fuel
denatured alcohol
isopropanol
2-ethoxyethanol
acetone
methylethylketone
NOR1 – candle/lamp oil
NOR2 – outdoor torch fuel
NOR3 – lamp oil
NOR4 – lamp oil
NOR5 – Norpar 12
NOR6 – Norpar 13
NOR7 – Norpar 14
NOR8 – Norpar 15
Isopar C
Isopar E
Isopar G
Isopar H
Isopar K
Isopar L
Isopar M
Isopar V
NAP1 – citronella torch fuel
Exxsol D80
Exxsol D110
Exxsol D130
100 type solvent
150 type solvent
aromatic 200 fluid