

Analysis of Gasoline Using Whole-Oil GC/MS: An Alternative to Methods Employing Sample Preparation

Mark J. Benotti*, Robert D. Lizotte, Kevin McInerney, and Jonathan Thorn – Battelle

INTRODUCTION

Analytical methods for the analysis of petroleum products include the measurement of the more volatile components by purge-and-trap gas chromatography mass spectrometry (GC/MS) and the larger molecular weight hydrocarbons by GC/MS and gas chromatography flame ionization detection (GC/FID). An alternative to this approach is analysis using a whole-oil method, in which sample is directly injected into the GC/MS or GC/FID without sample preparation. This approach provides a unique tool for the analysis of light to medium distillates and NAPL samples. Potential benefits of this approach may include 1) generation of a sample fingerprint by either full-scan GC/MS or GC/FID, 2) more accurate measurements of the compounds at the margins of volatility, and 3) mitigation of interference from solvent. This poster illustrates the applications of the whole-oil method on a set of gasoline samples collected throughout the United States. Differences in the composition of paraffin, isoparaffin, aromatic, naphthenic, and olefin compound classes vary in samples collected from the same brand but different geographic regions as well as in samples collected from the same geographic region but from different companies. This approach may be used to fingerprint light to medium distillates and NAPL samples in environmental forensic applications.

APPROACH

Eighteen gasoline and one diesel fuel samples were collected from different service stations in four locations throughout the United States (Figure 1). Each sample was analyzed by the whole-oil GC/MS method detailed in this work, and the data were compared to illustrate how this method may be used in forensic applications.

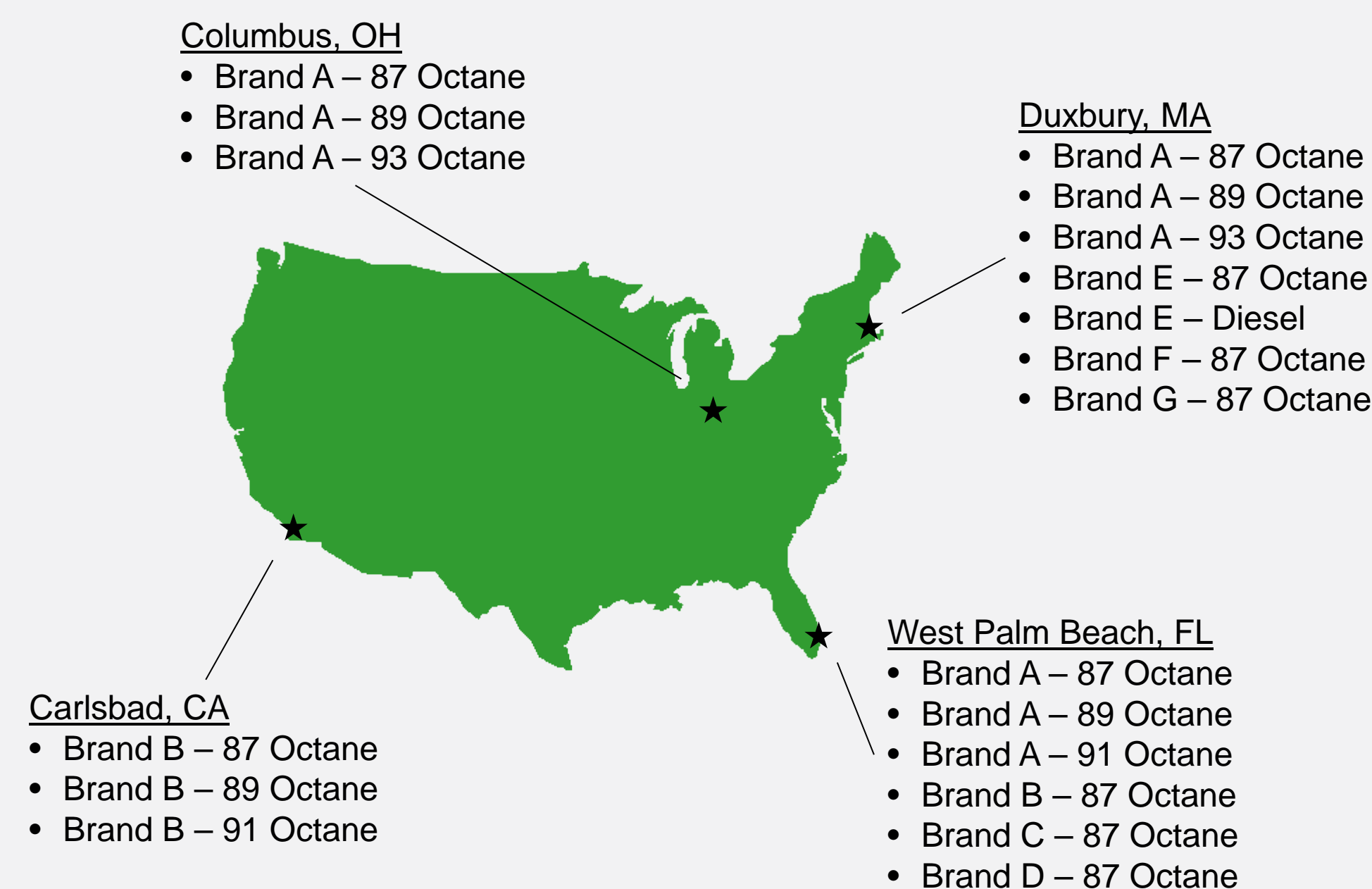


Figure 1: Locations and types of samples collected from four locations throughout the United States.

WHOLE-OIL GC/MS METHOD

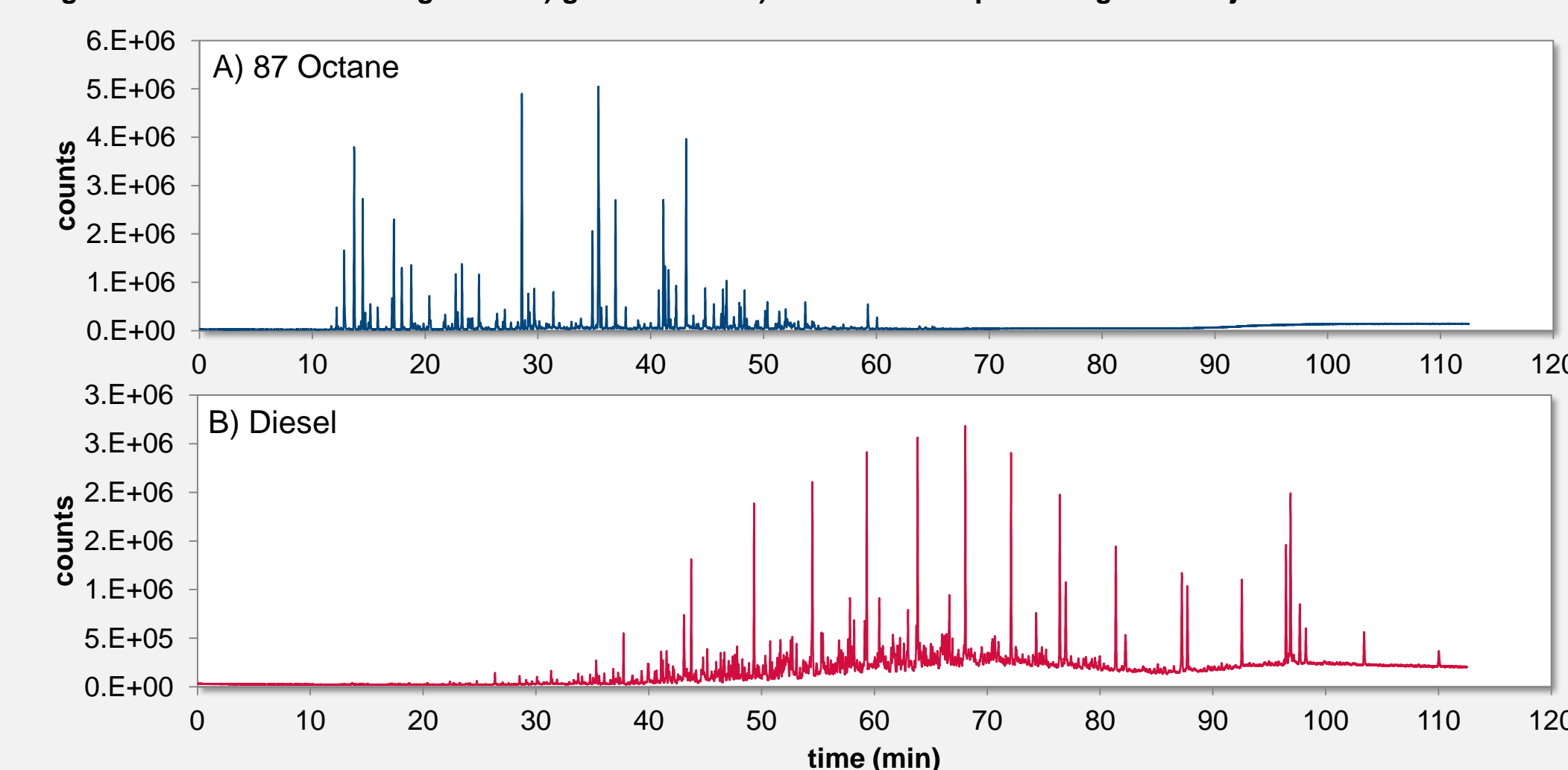
Methodology

- No sample preparation – 1 μ L of sample injected directly into GC/MS
- No internal standards – external calibration used to calculate concentration (see discussion below)
- Data acquired in full-scan mode (20-500 amu)
- Calibration curve generated using PIANO and alkane standards
 - 173 total analytes
- Quality Control (QC) samples to document contamination and precision
 - Performance blank to document contamination during analysis
 - Each sample run in triplicate to demonstrate precision (%RSD of detections <30%)

Discussion of Methodology

It is possible to use total ion chromatograms (TICs) to help identify different samples (e.g. Figure 2). In this case, the data are generated by full scan GC/MS using an external calibration, so care must be taken not to over-interpret. Due to different response factors of individual hydrocarbons, this approach would be useful for distinguishing different types of light- and middle-distillates from each other. Though the use of GC/MS may compromise some of the ability to use the TIC for identification, it does afford better compound identification through the availability of mass spectra and the ability to search them against mass spectral libraries. If this whole-oil approach was used with a GC/FID, then the trace may be used to distinguish like samples.

Figure 2: Full-scan chromatogram of A) gasoline and B) diesel fuel samples using direct-inject GC/MS method

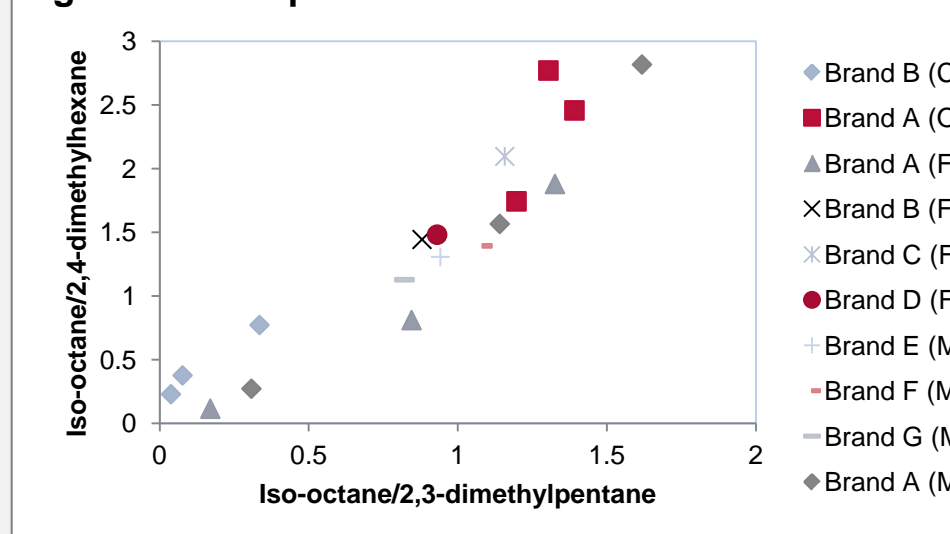


INTERPRETATION OF DATA FROM GASOLINE SAMPLES

Bulk chemical compositions of gasoline samples can be compared using radar plots to illustrate the different contributions of paraffin, isoparaffin, aromatic, naphthenic and olefin compound classes. As an illustrative example, Figure 3 shows the different PIANO concentrations in low-, middle- and high-grade gasoline in samples collected from the same brand in Ohio, Florida and Massachusetts. Aromatic compounds make up the largest fraction in all grades of the gasoline collected in Ohio, whereas isoparaffins make up the largest fraction in all grades from Florida.

This suggests that a single source (i.e. refinery) may have produced all the gas at the Ohio station or it is a custom blend specific to this region. Similarly, a different source produced all the gas at the Florida station or it is a custom blend specific to this region. At the Massachusetts station, the low and middle-grades are dominated by aromatic compounds similar to the Ohio gasoline samples, whereas the high-grade gasoline is dominated by isoparaffins similar to the Florida gasoline samples. Interestingly, four low-grade gasoline samples from four different brands in Florida (Figure 4) are dominated by isoparaffins.

Figure 5: Cross-plot of selected isoalkane ratios of gasoline samples



Depending on the need for and type of forensic approach, ratios of individual compounds can prove useful for identifying differences between samples. The presence of iso-alkane in all of these gasoline samples indicates the refiners all used an alkylation unit in the production of gasoline. However, differences in the ratio of iso-octane to other iso-alkanes may provide opportunity during a forensic investigation to distinguish between gasoline from different sources and/or different grades of gasoline. In Figure 5, the mid- and high-grade gasolines exhibit lower ratios of both iso-octane/2,4-dimethylhexane and iso-octane/2,3-dimethylpentane and therefore plot closer to the origin as compared to the low-grade gasolines from the same brand.

*corresponding author: 397 Washington Street, Duxbury, MA 02332 (781) 952-5250; benottim@battelle.org

CONCLUSIONS

Three gasoline samples were measured by purge-and-trap GC/MS and liquid-liquid extraction with GC/FID to illustrate how concentrations of analytes detected by both methods do not always agree. Figure 6 and Table 2 show differences in concentrations for compounds targeted by both methods likely due to different sample preparation. This phenomenon is mitigated with the whole-oil analysis as there is no sample preparation.

Figure 6: Comparison of the measured concentrations of the three alkanes measured by both methods.

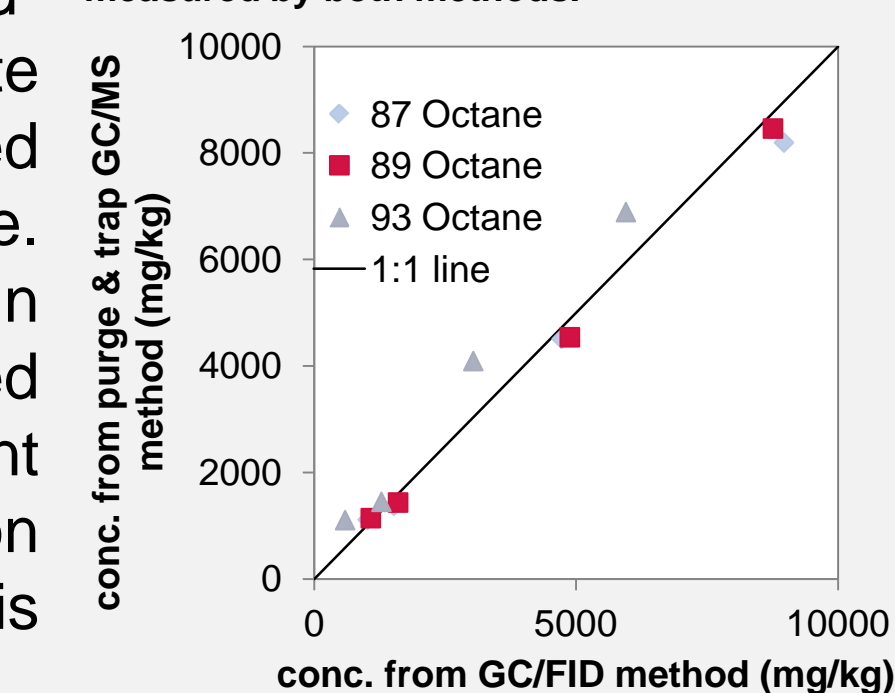


Table 2: Comparison of alkane concentrations measured by purge & trap (P&T) GC/MS and liquid-liquid extraction (LLE) GC/FID for three gasoline samples

	87 Octane		89 Octane		93 Octane	
	P&T GC/MS	LLE w/ GC/FID	P&T GC/MS	LLE w/ GC/FID	P&T GC/MS	LLE w/ GC/FID
n-Pentane	16000	-	62700	-	50300	-
n-Hexane	15500	-	48600	-	36000	-
n-Heptane	10600	-	27000	-	9580	-
n-Octane	11600	-	11300	-	7550	-
n-Nonane	8970	8200	8760	8460	5950	6900
n-Decane	4720	4510	4880	4540	3040	4090
n-Undecane	1520	1370	1600	1430	1280	1450
n-Dodecane	1020	1110	1080	1140	591	1100
n-Tridecane	-	435.3	-	471	-	437
n-Tetradecane	-	177.5	-	186	-	185
n-Pentadecane	-	117.6	-	123	-	128
n-Hexadecane	-	68.4	-	72.3	-	87.4

Conclusions

- Analysis of light- and middle distillates as well as NAPL samples by whole-oil GC/MS or GC/FID provides an alternative approach to hydrocarbon analysis
- The method is not susceptible to volatility loss as may occur with purge-and-trap or liquid-liquid extraction sample preparation
- When used with GC/MS, data and TICs must be carefully regarded given differences in the response factors of individual analytes
- Using this approach, differences in the composition of different grades of gasoline collected at locations throughout the US were noted indicating different sources or differences in blends

Future Work

- Standardize GC/MS data against a material with known amounts of hydrocarbons to mitigate the uncertainty due to variable response
- Develop library of whole-oil GC/FID data for light- and middle-distillates for the identification of NAPL and other unknown samples in forensic applications
- Assess viability of using this method for crude oil samples

ACKNOWLEDGEMENT

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