FINAL REPORT

GC×GC STUDIES OF PALETTE COMPOUNDS USED IN THE NEXT GENERATION OF DIESEL FUEL SURROGATE BLENDS

R. Gieleciak
Natural Resources Canada, CanmetENERGY in Devon

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EXECUTIVE SUMMARY

Through the PERD 113 (p-001896.001) and ecoEII (p-001390.001) projects, CanmetENERGY collaborated with the US Department of Energy and the Coordinating Research Council (CRC) to develop methods to better characterize transportation fuels and in order to correlate detailed fuel chemistry with physical properties and ultimately with internal combustion engine performance.

CRC sought the help of CanmetENERGY to estimate the purities of standard model compounds proposed for use in making surrogates of diesel fuel blends for CRC's AVFL-18a project. These surrogates are used in the development of detailed chemical kinetic models of diesel fuels in fuel combustion research. Comprehensive two-dimensional gas chromatography (GC×GC) with various detector types was used to carry out all component purity analyses.

This report documents the results of the detailed determination of purity of 13 surrogate palette compounds involved in the preparation of the CRC AVFL-18a second generation surrogate diesel fuels. The analytical results reported for each sample include the content of the main compound as well as detected contaminants (in weight percentage).

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ABBREVIATIONS/DEFINITIONS

1MN	1-methylnaphthalene
2MHPD	2-methylheptadecane
AVFL	Advanced Vehicle, Fuel, and Lubricants
CFA	2007 #2 ULSD emissions certification fuel, batch A
CN	cetane number (ASTM D613)
CRC	Coordinating Research Council (www.crcao.org)
DCN	derived cetane number (ASTM D7170)
ES	Eastern Sources (www.easternsources.com)
FACE	Fuels for Advanced Combustion Engines
FID	flame ionization detection
FIMS	field ionization mass spectrometry
FS	Fisher Scientific (www.fishersci.com)
GC×GC	comprehensive two-dimensional gas chromatography
HMN	2,2,4,4,6,8,8-heptamethylnonane
NBCX	*n*-butylcyclohexane
NEI	*n*-eicosane
NIST	U.S. National Institute of Standards and Technology
NHXD	n-hexadecane
NMR	nuclear magnetic resonance spectroscopy
NOD	*n*-octadecane
NRC	National Research Council of Canada
PHP	perhydrophenanthrene
PNNL	Pacific Northwest National Laboratory
SA	Sigma-Aldrich (www.sigmaaldrich.com)
SCD	sulfur chemiluminescence detector
Surrogate fuel	fuel composed of a small number of pure components that is formulated to match selected properties of a target fuel
Target fuel	a ‘real’ fuel with selected properties that are to be matched by a surrogate fuel
TDEC	*trans*-decalin
TET	tetralin

TIPB	1,3,5-triisopropylbenzene
TIPCX	1,3,5-triisopropylcyclohexane
TMB	1,2,4-trimethylbenzene
TOF-MS	time-of-flight mass spectrometry
T90	temperature at which 90 vol% of fuel is distilled
ULSD	ultra-low sulfur diesel fuel

1.0 BACKGROUND

Substantial improvements in diesel engine efficiency and GHG emission footprints are required to meet future legislation goals, especially with respect to global decisions made recently at the Paris Climate Change Conference in November 2015 (1). However, the conventional engine ‘build-and-test’ approach, based on development and optimization of engine prototypes, is too expensive and time-consuming to meet these challenges. The complex chemical nature of modern diesel fuels results in ever more challenging tasks related to identification, description, interpretation, and modeling of the relationships between fuel composition and engine combustion.

These facts led to a simplification of the problem by the use of surrogate fuel mixtures in such studies (2-4). A surrogate fuel is defined as a fuel composed of a small number of pure compounds (known as palette compounds) that match selected characteristics of a target fuel which is composed of many compounds (i.e. hundreds to thousands of species). The development of surrogate fuels is complicated because they must be formulated in such a way as to mimic as accurately as possible the behavior of the target fuel during the injection, vaporization, mixing, and combustion processes occurring in engines (2,3). Figure 1 presents the distinction between surrogate and target fuels.

After formulation, the surrogate fuels are typically submitted to a broad range of advanced engine research and combustion vessel experiments to investigate the impact of chemical composition on engine performance, followed by computational combustion modeling using a combination of computational fluid dynamics (CFD) and detailed chemical kinetics.

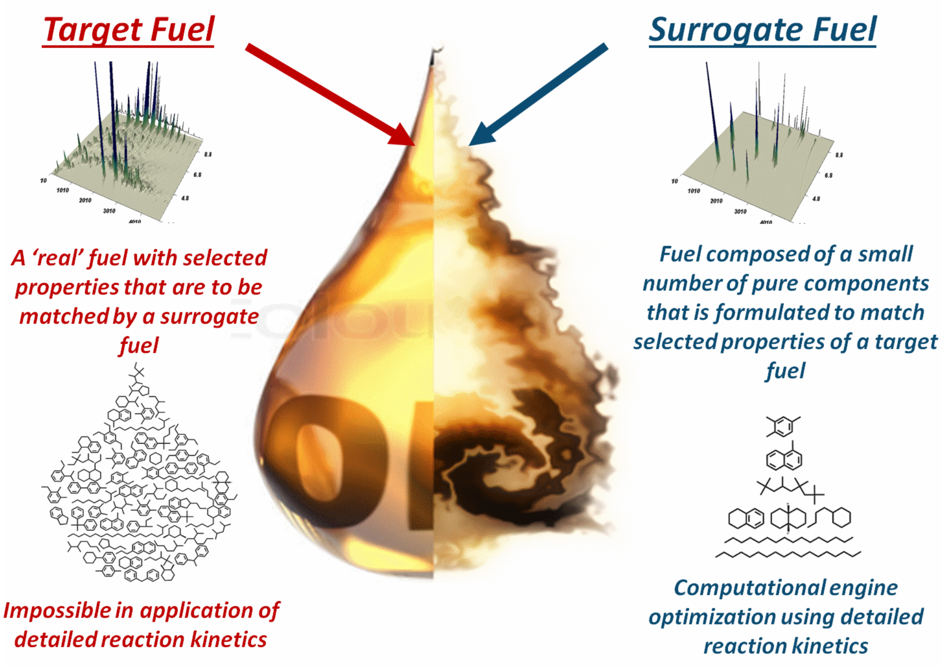


Figure 1 – Schematic explaining differences and similarities between target and surrogate fuels

In the current study, performed in support of the Coordinating Research Council (CRC) Advanced Vehicle/Fuel/Lubricants (AVFL) committee project entitled '*Surrogate Fuels for Kinetic Modeling*' (Project AVFL-18a) (5), CanmetENERGY in Devon provided a detailed hydrocarbon profiling of standard diesel fuel, the surrogate fuels formulated and blended by the CRC AVFL-18a working group, as well as the model compounds used during formulation of the second generation of surrogate fuels.

2.0 INTRODUCTION

Before a surrogate palette component is used in any experimental or modeling study, basic information about its chemical, physical and thermophysical properties, and especially about its purity is needed (2, 3). Otherwise, the properties of the surrogate fuel could be biased by the unknown contaminants existing in the palette compound.

Organic compounds are either synthesized or isolated from natural sources. Usually, it is difficult or even impossible to obtain chemicals in absolutely pure form. The sources of impurities in chemical standards can vary and include residual starting materials, side-products of synthesis, degradation products formed during storage, and contaminants added at some point during compound management. Typically suppliers report the impurity level expressed as mass

% purity but they do not provide details about the nature of the contaminants (e.g., compound name, the number of types of species, etc.).

The acceptable level of contamination of model compounds strongly depends on the purpose and application for the compound. For instance, the presence of impurities in trace quantities in drug products can be responsible for teratogenic, mutagenic, or carcinogenic effects on the human body (6). All engineering materials contain a trace level of impurities, which can play a major role in the observed changes in mechanical properties of the material (7, 8). In the petroleum industry, exact measurement of certain key physicochemical properties such as density, viscosity, T90, etc. is not sensitive to the exact level of impurities. On the other hand, experimental values for properties such as cetane number, cloud point or lubricity can be significantly affected by parts-per-million (ppm) levels of contamination. For example, trace quantities of peroxides in diesel fuels can act as promotors of autoignition reactions and lead to increased cetane number values of those fuels (2, 9). It was shown that impurities such as glycerols, free fatty acids (FFAs), metals, and unsaturates in biodiesels may detrimentally affect fuel stability and engine performance (10, 11).

The work presented in this report is similar in nature to the study carried out at CanmetENERGY in 2010 (12). The purity levels of compounds reported in the aforementioned report were taken into account during CRC's formulation of the first generation of surrogate fuels (5). In the current study, performed in support of the CRC project AVFL-18a entitled '*Surrogate Fuels for Kinetic Modeling*', CanmetENERGY provided (a) a detailed hydrocarbon impurity profile for each palette compound, and (b) advanced hydrocarbon compositions of mixtures used during formulation of the second generation of surrogate fuels. The recent palette developed by CRC contains 13 compounds including new species custom synthesized and/or purified by Eastern Sources (13) and Sigma-Aldrich (14).

All of the chemical analyses provided in this report were performed using two-dimensional gas chromatography (GC×GC), a technique described in many internal reports (e.g., 9, 15) and scientific papers (e.g., 16).

3.0 EXPERIMENTAL

3.1 SAMPLES

All model compounds investigated in this study were procured by CRC project AVFL-18a. The list of 13 palette compounds, used in the preparation of the four surrogate fuels, their manufacturing sources, and their stated purities are presented in Table 1. The compounds are grouped according to their respective hydrocarbon types.

Table 1 – Compound names, abbreviations, and stated purities (by supplier)

No	**Compound Name**	**Compound ID**	**Stated purity (wt%)**	**Supplier** [a]
n-alkanes				
1	*n*-hexadecane	NHXD	99	FS
2	*n*-octadecane	NOD	99	SA
3	*n*-eicosane	NEI	99	SA
iso-alkanes				
4	2,2,4,4,6,8,8-heptamethylnonane	HMN	98	FS
5	2-methylheptadecane	2MHPD[b]	>98	ES
Cycloalkanes				
6	*n*-butylcyclohexane	NBCX	>99	TCI
7	1,3,5-triisopropylcyclohexane	TIPCX [b]	>98	(ES, SA)
8	*trans*-decalin	TDEC	>98	TCI
9	perhydrophenanthrene	PHP [b]	>98	(ES, SA)
Naphtheno-aromatics				
10	tetralin	TET	99	SA
Aromatics				
11	1,2,4-trimethylbenzene	TMB	>98	FS
12	1,3,5-triisopropylbenzene	TIPB [b]	>98	SA
13	1-methylnaphthalene	1MN [b]	>98	ES

[a] ES = Eastern Sources (www.easternsourcess.com/), FS = Fisher Scientific (www.fishersci.com), SA = Sigma-Aldrich (www.sigmaaldrich.com), and TCI = TCI America (http://www.tcichemicals.com/)

[b] Custom synthesis

The palette compounds are shown in Figure 2 and Figure 3, the former figure presenting two-dimensional depictions and the latter figure showing geometrically-optimized structures.

Selected physical properties for most of the palette compounds measured by members of CRC's AVFL-18a project panel are provided in Appendix A. Properties for newly synthesized compounds such as TIPCX or PHP are limited to density and boiling point and will be investigated in the future.

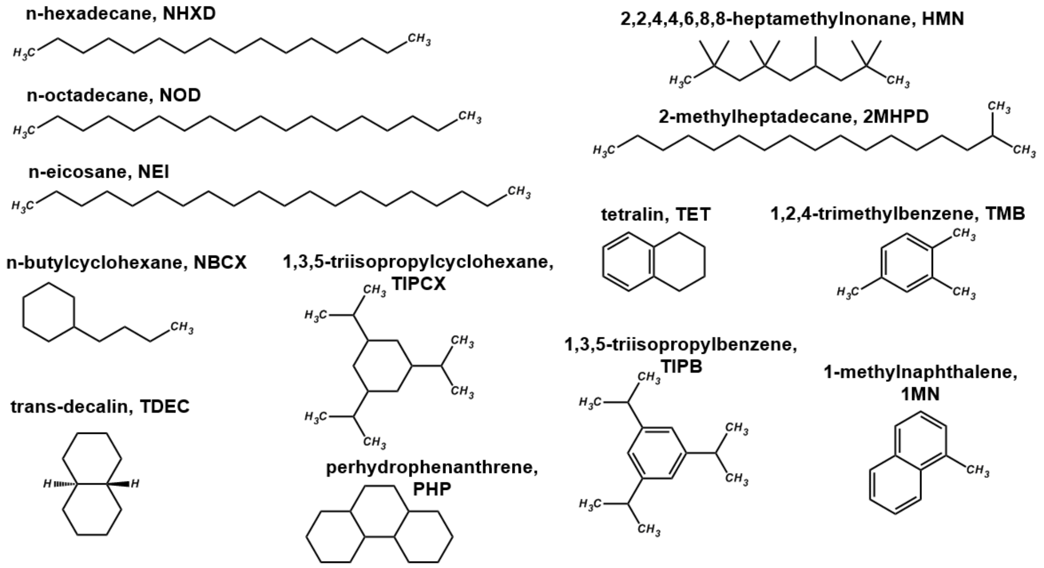


Figure 2 – 2-D representations of surrogate palette compounds submitted for purity analysis

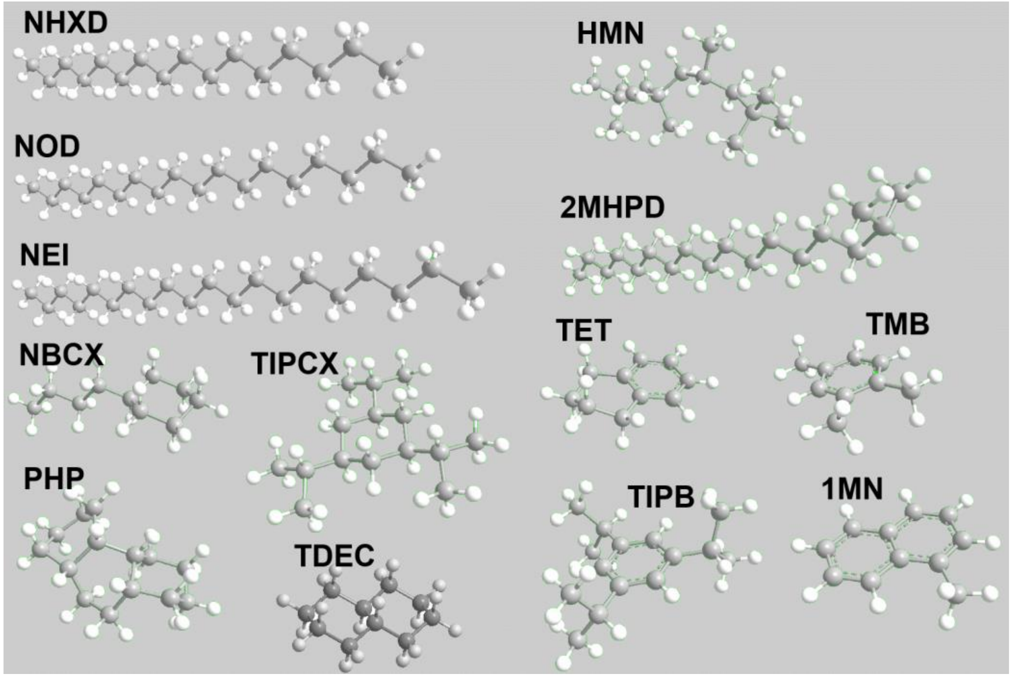


Figure 3 – 3-D representations of surrogate palette compounds submitted for purity analysis

In addition to the determination of the purities of the model compounds presented in Table 1, CanmetENERGY in Devon analyzed the hydrocarbon composition of the four surrogate fuels in order to verify that were prepared correctly.

3.2 INSTRUMENTATION

An Agilent 6890N gas chromatograph (Agilent Technologies, Mississauga, Canada) equipped with a thermal modulator (Leco Instruments, Mississauga, ON, Canada) and secondary oven was used for the analyses presented in the report. This instrument has two detectors (FID and SCD) arranged in a tandem configuration. Hence, in addition to the common hydrocarbon response, there one can obtain information about sulfur species (if any). The column features and the operating conditions are listed in Table 2.

Table 2 – Experimental setup for GC×GC analysis

	GC×GC-FID/SCD	**GC×GC-TOFMS**
1st column	VF5-HT, 30 m x 0.32 mm DF:0.1	VF17-MS, 30 m x 0.32mm DF:0.1
Main oven program	50 °C (1) to 290 °C (0) at 5 °C/min	50 °C (1) to 340 °C (0) at 5 °C/min
2nd column	BPX-50, 1.0 m x 0.1 mm DF:0.1	VF5-HT,1.5 m x 0.1 mm DF:0.2
Secondary oven program	10 °C offset from the main oven	40 °C offset from the main oven
Inlet Temperature	350 °C	350 °C
Injection size	0.1 μL	0.2μL
Split ratio	200:1	40:1
Carrier gas	He, constant flow, 1.5 mL/min	He, constant flow, 1.5 mL/min
Modulator temperature	55 °C offset from the main oven	55 °C offset from the main oven
Detector	FID, 350 °C with SCD adapter, 800 °C	TOFMS
Acquisition rate	100 Hz	100 Hz
Modulation period	4 s	8 s

In addition to the GC×GC-FID/SCD analysis, which provides quantitative information, we ran experiments on a second GC×GC instrument equipped with a time-of-flight mass spectrometer (TOFMS) detector, which is very useful in providing structural information of the chemical species. The column features and operating conditions for GC×GC-TOFMS are listed in Table 2.

3.3 METHODOLOGY

Palette compound samples were dispensed into GC vials. All samples, except for *n*-octadecane and *n*-eicosane (solids that were dissolved in dichloromethane), were injected neat into the GC×GC system under the chromatographic conditions shown in Table 2. The total GC×GC separation analysis time depended on the nature of the separated analytes; boiling point was a limiting parameter.

Data handling, such as contour plotting, GC×GC peak collection, retention time measurements, and peak volume calculation were performed using ChromaTOF software, from Leco Instruments. Chemical compounds were identified by searching for matching spectra in U.S. National Institute of Standards and Technology (NIST) mass spectral libraries. All quantitative analyses were based on FID output and are reported as average values from all GC×GC-FID experiments performed on the samples (both neat and diluted in DCM). Results for each compound are shown as percentages of the total area of the quantified peaks, which in the case of FID is equivalent to weight percent (wt%).

The sulfur chemiluminescence detector (SCD) allows for very sensitive and extremely selective detection of substances that contain sulfur. If the molecular weight of the sulfur-containing compound is known, quantitative determination of the compound, down to very low concentrations, is possible.

4.0 RESULTS AND DISCUSSION

4.1 SURROGATE PALETTE COMPOUNDS

Two-dimensional gas chromatography was used for both quantitative and qualitative analysis. Sulfur chemiluminescence detection was utilized for identification and quantification of impurities containing sulfur. The GC×GC-TOFMS technique allowed us to confirm the identity of the main component, estimate the molecular structure of contaminants, or, in more difficult cases, to simply assign the impurities to one of the main hydrocarbon type groups. Table 3 includes results from these analyses. More detailed results, including both two-dimensional chromatograms and impurity characteristics, are described in the next few sections.

Table 3 – GC×GC-FID results for purity estimation of surrogate palette compounds

No	**Compound Name**	**Stated purity (wt%)**	**GC×GC-FID (area %)**
1	*n*-hexadecane	99	99.1
2	*n*-octadecane	99	99.3
3	*n*-eicosane	99	98.9
4	2,2,4,4,6,8,8 – heptamethylnonane	98	99.1
5	2-methylheptadecane	>98	98.5
6	*n*-butylcyclohexane	>99	99.8
7	1,3,5-triisopropylcyclohexane	>98	98.6
8	*trans*-decalin	>98	99.5
9	Perhydrophenanthrene	>98	98.7
10	Tetralin	99	99.2
11	1,2,4-trimethylbenzene	>98	99.2
12	1,3,5-triisopropylbenzene	>98	98.1
13	1-methylnaphthalene	>98	99.5

The results in the following sections include:

- GC×GC chromatograms of regions of interest where both major compound peaks and contaminants are shown; the intensities of the signals were enhanced by lowering the color threshold to highlight and facilitate visualization of impurity peaks coexisting with the major compound.
- The result table - reporting content and type of compounds found in the sample. With regard to contaminants, in a few cases, accurate name attribution to the detected peak was impossible because of the low content of the analyte or the lack of an appropriate mass spectrum in the NIST MS library.
- A short discussion of the results.

Selected mass spectra acquired from the TOFMS detector are presented in the appendices.

4.1.1 NORMAL ALKANES

***N*-hexadecane, *n*-octadecane, and *n*-eicosane**

Three normal alkanes, *n*-hexadecane, *n*-octadecane, and *n*-eicosane, were selected by the CRC AVFL-18a project panel as representatives of paraffinic hydrocarbons used in the formulation of diesel fuel surrogates. Structures of the *n*-paraffins are presented in Figure 2. The heaviest alkane molecule in the palette, *n*-eicosane, was used to better match the heavy end of the surrogate fuel distillation curve.

Figure 4 presents GC×GC-FID chromatograms of normal alkane compounds submitted for purity testing. In general, all three compounds were characterized by high purity, close to or exceeding the purity levels stated by the supplier. The color axis indicating concentration was enhanced to visualize the low impurity concentrations in these samples. Peak retention times increased with increasing chain length of the major component, which is expected as the boiling point of these species increase with increasing size. For all cases presented in Figure 4, the impurities were scattered around major *n*-paraffinic compounds giving a characteristic pattern. Each major compound is surrounded by isoparaffins with lower and higher carbon atoms. Most of the species were run on GC×GC-TOFMS to confirm the structure of the major compound as well as the contamination species.

Table 4 reports the contents of major compounds and contaminants found in the samples.

Table 4 – GC×GC-FID quantitative results for normal alkanes (based on three experiments)

ID	Major compound name (area% ± SD)	Contaminations (area%)	Reference to Figure
NHXD	*n*-hexadecane (99.11 ± 0.02)	(A) C16-isoparaffins (0.63); (B) C16-cycloparaffins (0.08); (C) C17-isoparaffins (0.10); unknown (0.09)	Figure 4a
NOD	*n*-octadecane (99.32 ± 0.02)	(A) C18-isoparaffin (0.29); unknown (0.39)	Figure 4b
NEI	*n*-eicosane (98.90 ± 0.01)	(A) C20-isoparaffins (0.21); (B) C20-isoparaffins (0.43); (C) C21-isoparaffins (0.21); unknown (0.27)	Figure 4c

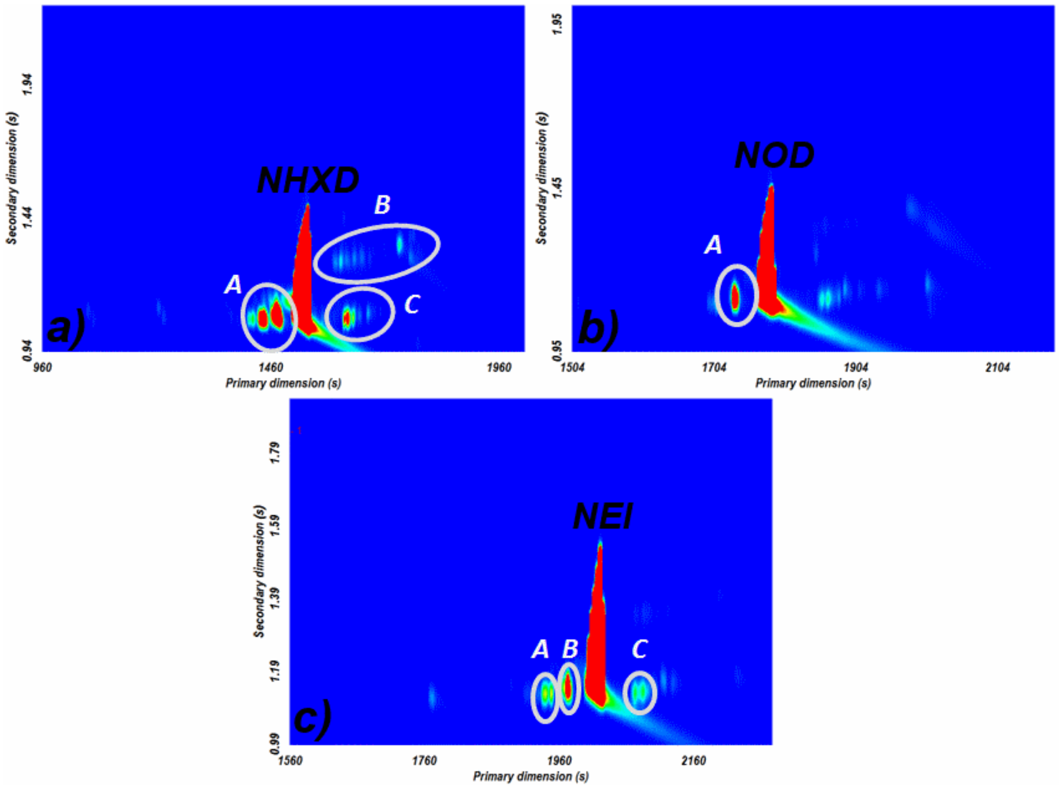


Figure 4 – GC×GC-FID chromatograms of *n*-hexadecane (a), *n*-octadecane (b), and *n*-eicosane (c). A, B, and C – are the labels of the impurity peaks (see Table 4)

4.1.2 BRANCHED ALKANES

2,2,4,4,6,8,8 – heptamethylnonane (HMN)

2,2,4,4,6,8,8 – heptamethylnonane (aka isocetane) is the first of two branched alkanes used in the preparation of surrogate diesel fuels. HMN is a structural isomer of *n*-hexadecane and as such has the same molecular formula, $C_{16}H_{34}$. However, due to its highly branched structure (see Figure 2) the physical properties of this compound are anticipated to be very different than those of its counterpart, straight chain *n*-hexadecane (NHXD). For example the boiling point of HMN is about 40 °C lower than that of NHXD (see Appendix A). The purity of HMN was high (99.1 wt% - see Table 5), and was significantly higher than the purity reported by the manufacturer (98 wt% - Fisher Scientific). The impurities constituted about 0.9 wt% and were distributed across ~20 species. Most were isoparaffins and olefins. One of the major contaminants was the compound located in the low retention time part of the GC×GC chromatogram (see Figure 5). Based on its mass spectrum and the spectral library the compound was the highly substituted paraffin 2,2,4,6,6-pentamethylheptane.

Table 5 – GC×GC-FID quantitative results for 2,2,4,4,6,8,8 – heptamethylnonane sample (based on 3 experiments)

ID	Major compound name (area% ± SD)	Contaminant (area%)
MHN	2,2,4,4,6,8,8 – Heptamethylnonane (99.10 ± 0.05)	(A) 2,2,4,6,6-pentamethylheptane (0.31); unknown (0.59)

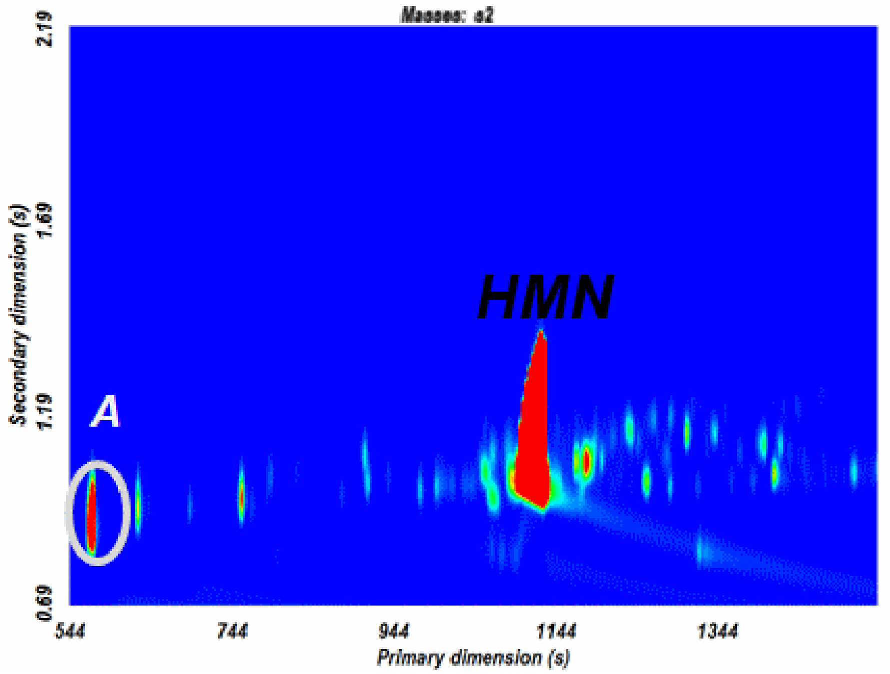


Figure 5 – GC×GC-FID chromatogram of 2,2,4,4,6,8,8 – heptamethylnonane (HMN).

Figure 6 presents the mass spectrum of HMN, which is very characteristic for highly branched paraffins. Chain branching causes a decrease in $[M^{\cdot+}]$ and a characteristic increase in the abundances of $C_nH_{2n+1}^+$ fragments (the high abundance of m/z=57 arise from $(CH_3)_3C^+$ fragments).

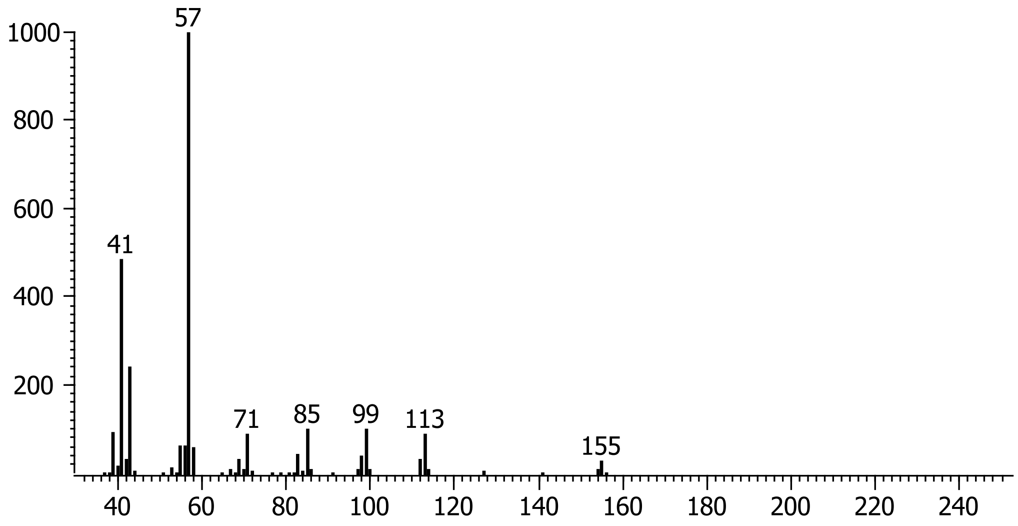


Figure 6 – Mass spectrum of 2,2,4,4,6,8,8 – heptamethylnonane based on TOFMS measurement

2-methylheptadecane (2MHPD)

It was found previously (17) that compounds containing quaternary carbon atoms (such as HMN which has three quaternary atoms) are rare in petroleum streams. It is accepted that moderately branched paraffins dominate over highly-branched paraffins (18). Therefore 2-methylheptadecane (2MHPD) was selected by CRC's AVFL-18a project panel to replace HMN in one of the surrogate fuels as it has a more representative structure than HMN regarding the types of branched alkanes found in commercial diesel fuels (3). Another reason to investigate 2MHPD as a potential palette compound and replacement for HMN was its reasonable price in comparison to other one-methyl substituted alkanes. The starting material for 2MHPD synthesis (methyl palmitate) is relatively inexpensive. 2MHPD was custom synthesized by Eastern Sources Inc. with the final cost of ~$5000 per kg.

2MHPD was provided in two batches: AP-74-1 and AP-82-5. Figure 7 presents the GC×GC-FID chromatograms of both samples. In general 2MHPD from the second batch (i.e. AP-82-5) was slightly more contaminated than AP-74-1. Quantitative results are shown in Table 6. Due to operational issues the samples were not investigated by GC×GC-TOFMS so the identification of the impurity is not known.

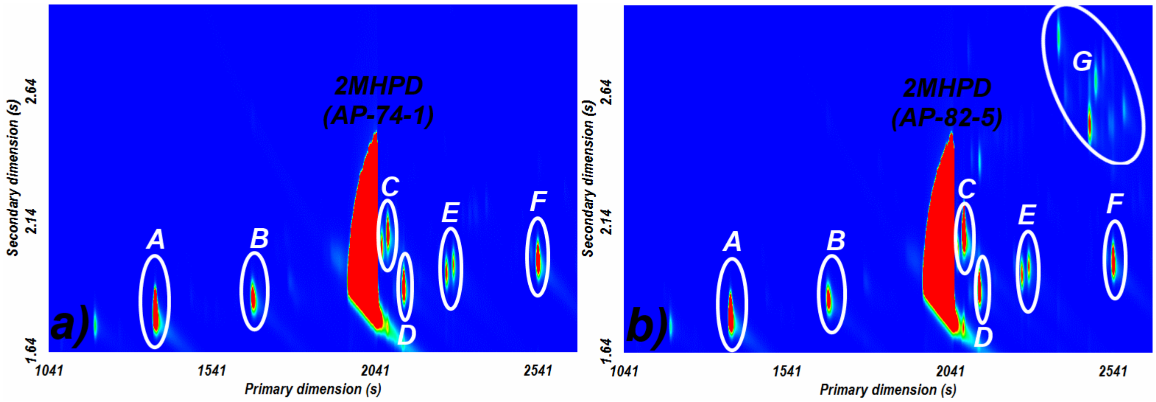
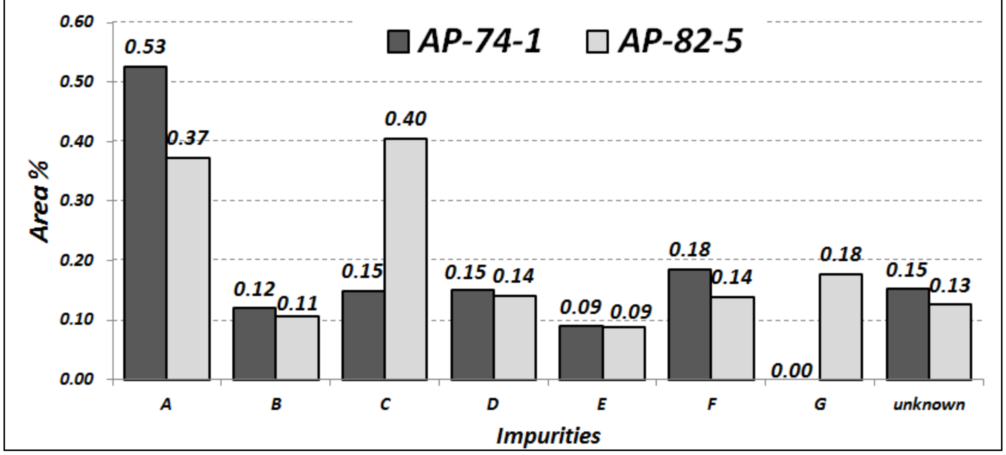


Figure 7 – GC×GC-FID chromatograms of 2MPHD from two different batches: AP-74-1 (a), AP-82-5 (b)

Table 6 – GC×GC-FID quantitative results for 2MHPD (based on two experiments)

	AP-74-1 (area % ± SD)	**AP-82-5 (area % ± SD)**
2-methylheptadecane	98.63 ± 0.02	98.45 ± 0.02
		

4.1.3 NAPHTHENES

Naphthenes (cycloparaffins) are important chemical components of distillate streams such as jet and diesel fuels. In contrast to paraffins, the ring structure of naphthenes introduces complex reaction pathways. Although progress has been made in the kinetic description of naphthene reactions, more work is needed to cover the full carbon range of this compound family

(4). Also, there is limited availability of high-purity naphthenes at reasonable prices, even for the relatively small quantities needed in fundamental combustion experiments.

N-butylcyclohexane (NBCX)

Information on the combustion behavior of naphthenes with longer alkyl side chains is required to simulate the combustion behavior of fuels (3). NBCX has been identified as a possible representative of long alkyl-chain substituted cycloparaffins. N-butylcyclohexane appeared to be the highest purity palette compound, containing only 0.15 wt% of contaminants (see Figure 8 and Table 7).

Table 7 – GC×GC-FID quantitative results for *n*-butylcyclohexane (based on three experiments)

ID	Major compound name (area% ± SD)	Contaminations (area%)
NBCX	*n*-butylcyclohexane (99.84 ± 0.02)	(A) 1-methyl-3-propylcyclohexane (0.07); (B) C16 cycloparaffin (0.03); (C) C16 cycloparaffin (0.02); unknown (0.04)

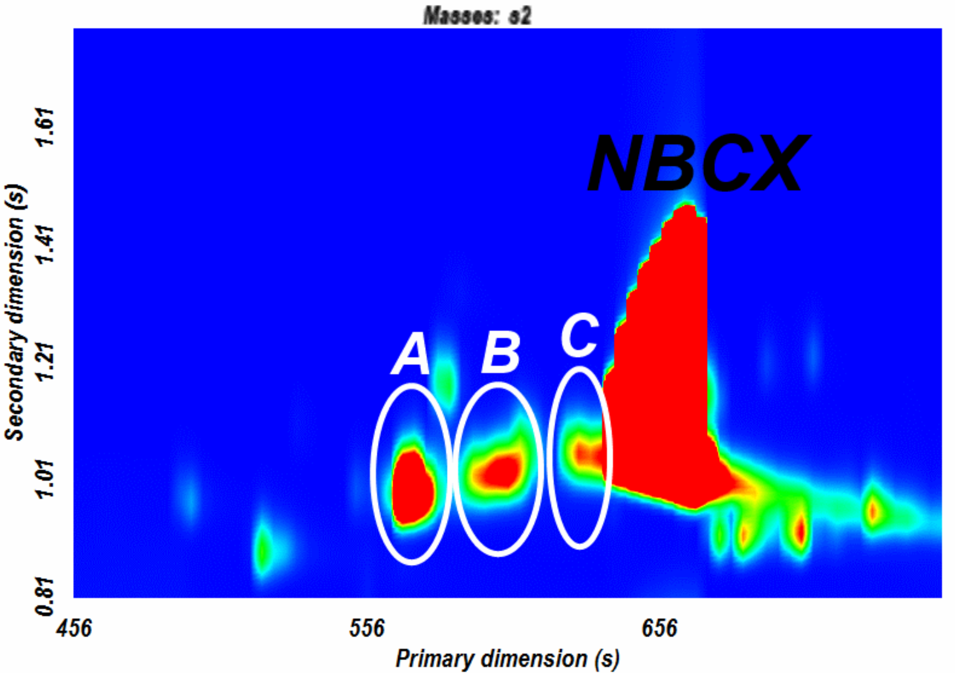
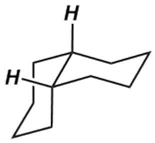
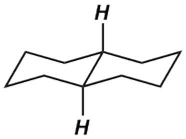


Figure 8 – GC×GC-FID chromatogram of *n*-butylcyclohexane

***Trans*-decalin (TDEC)**

Decalin has been identified as a multi-ring naphthene class surrogate component for both jet and diesel fuels (4) and has shown favorable combustion characteristics in both gas turbines and diesel engines (19, 20). As shown in Table 8, decalin exists in two stereoisomeric forms (*cis*- and *trans*-) which have different physical and chemical properties (21). Of the two isomers, *trans*-decalin is energetically more stable because of lower steric interactions. The two decalin isomers have very different ignition characteristics. The derived cetane number (DCN) of *cis*-decalin was found to be almost 10 units higher than that for *trans*-decalin.

Table 8 – Comparison of physical properties for decalin stereoisomers

Properties	***cis*-decalin**	***trans*-decalin**
Structure		
Boiling Point	193 °C	185 °C
Melting Point	-43 °C	-32 °C
Density	0.897 g/ml at 25 °C	0.87 g/ml at 25 °C
Refractive Index	n20/D 1.481	n20/D 1.469
DCN	41.6	32

Commercial decalin is a mixture of *cis*- and *trans*- isomers (typically in the ratio 77:23) and costs about 78 USD per liter (99 wt%). As such, decalin is one of the least expensive two-ring cycloparaffin compounds available on the market. However, each individual isomer is at least eight times more expensive than the mixture of isomers.

Figure 9 and Table 9 present the results of the GC×GC-FID analysis carried out on the *trans*-decalin sample. *Trans*-decalin is relatively pure. One of the major contaminants is the other isomer, *cis*-decalin. *Cis*-decalin has a higher boiling point than *trans*-decalin (see Table 8). Therefore, with the present column setup, the *cis* isomer is eluted later than its *trans* counterpart.

Table 9 – GC×GC-FID quantitative results for *trans*-decalin (based on three experiments)

ID	Major compound name (area% ± SD)	Contaminations (area%)
TDEC	*trans*-decalin (99.52 ± 0.02)	(A) *cis*-decalin (0.42); unknown (0.06)

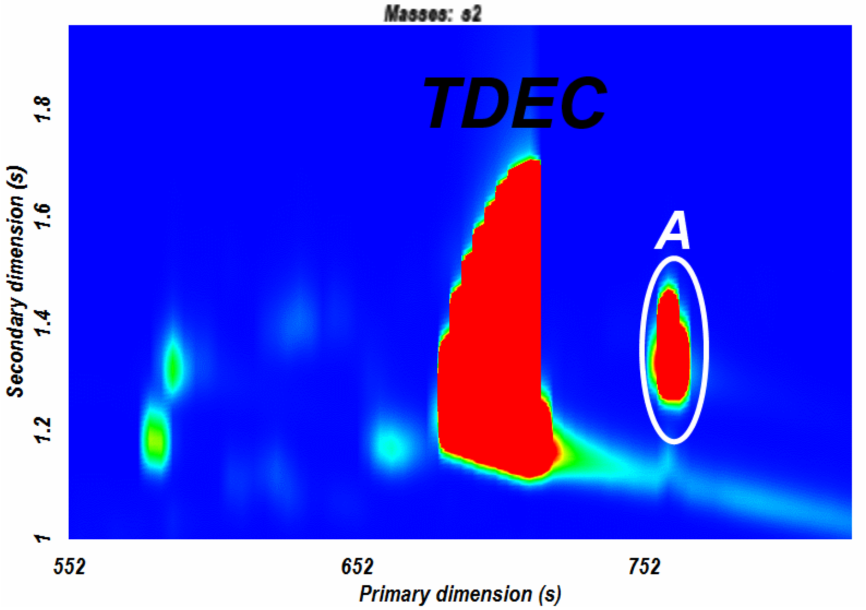


Figure 9 – GC×GC-FID chromatograms of *trans*-decalin

1,3,5-triisopropylcyclohexane (TIPCX)

The development of surrogate diesel fuel indicated the need for a multiply-substituted, low cetane number, high molecular mass monocycloalkane surrogate mixture component (12). 1,3,5-triisopropylcyclohexane was chosen as a palette component to serve these needs. This compound is not available commercially and was custom-synthesized by Eastern Sources (13) and Sigma-Aldrich (14) at CRC’s request. The synthesis involved catalytic hydrogenation of the corresponding substituted aromatic ring compound (i.e., 1,3,5-triisopropylbenzene). After purification the products were sent to CanmetENERGY for GC×GC-FID analysis.

In both cases, two major peaks were observed in the chromatograms as well as two sets of low-intensity peaks that eluted before and after the major peaks, as seen in Figure 10. The two major peaks were baseline resolved; the first, more abundant component eluted at a retention time (RT) of 2338 s and the second component at a RT of 2348 s.

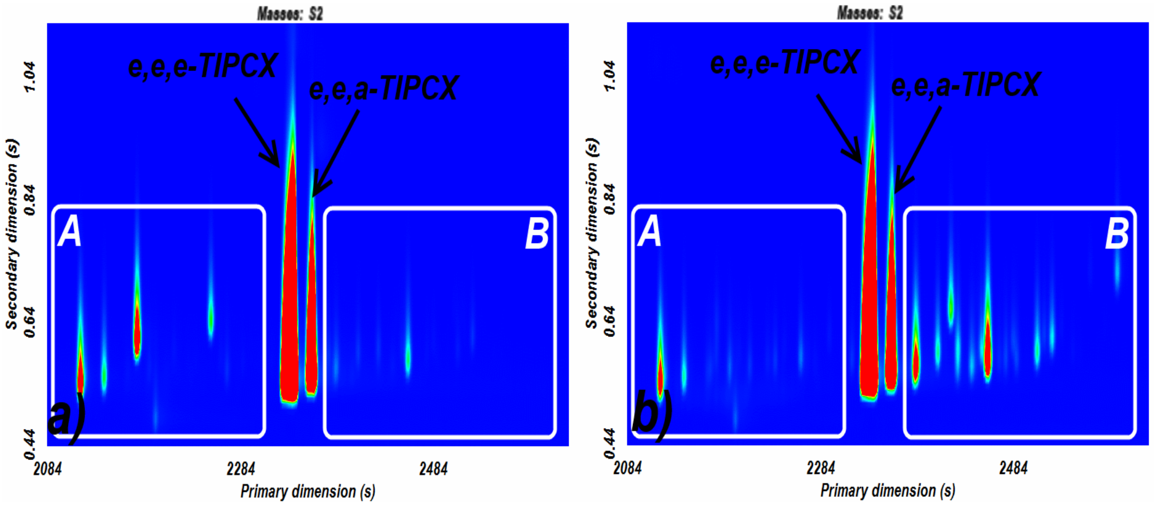


Figure 10 – GC×GC-FID chromatograms of *1,3,5-triisopropylcyclohexane* synthesized by Eastern Sources (a) and Sigma-Aldrich (b). Areas A and B show contamination peaks belonging to lower and higher boiling point compounds, respectively.

Based on the mass spectra obtained for these peaks and NMR spectra reported in (22), the peaks were attributed to different geometric stereoisomers of 1,3,5-triisopropylcyclohexane; *e,e,e* – and *e,e,a*- isomers, respectively. These isomers are presented in Figure 11, both as 2D and 3D molecular representations. The *e,e,e* -geometry isomer is expected to be thermodynamically more stable than its *e,e,a* counterpart due to a lack of steric hindrance of the bulky isopropyl group located in the axial position. A simple comparison of final heats of formation calculated by the author for both isomers using AM1 Hamiltonian (included in the AMPAC software package (22)) seems to confirm this assumption (ΔH_f (*eee*) = -81.49 kcal/mol vs. ΔH_f (*eea*) = -79.64 kcal/mol). The major product was assigned to the *e,e,e* -geometry and the minor product to the *e,e,a* - geometry of the substituents around the cyclohexane ring.

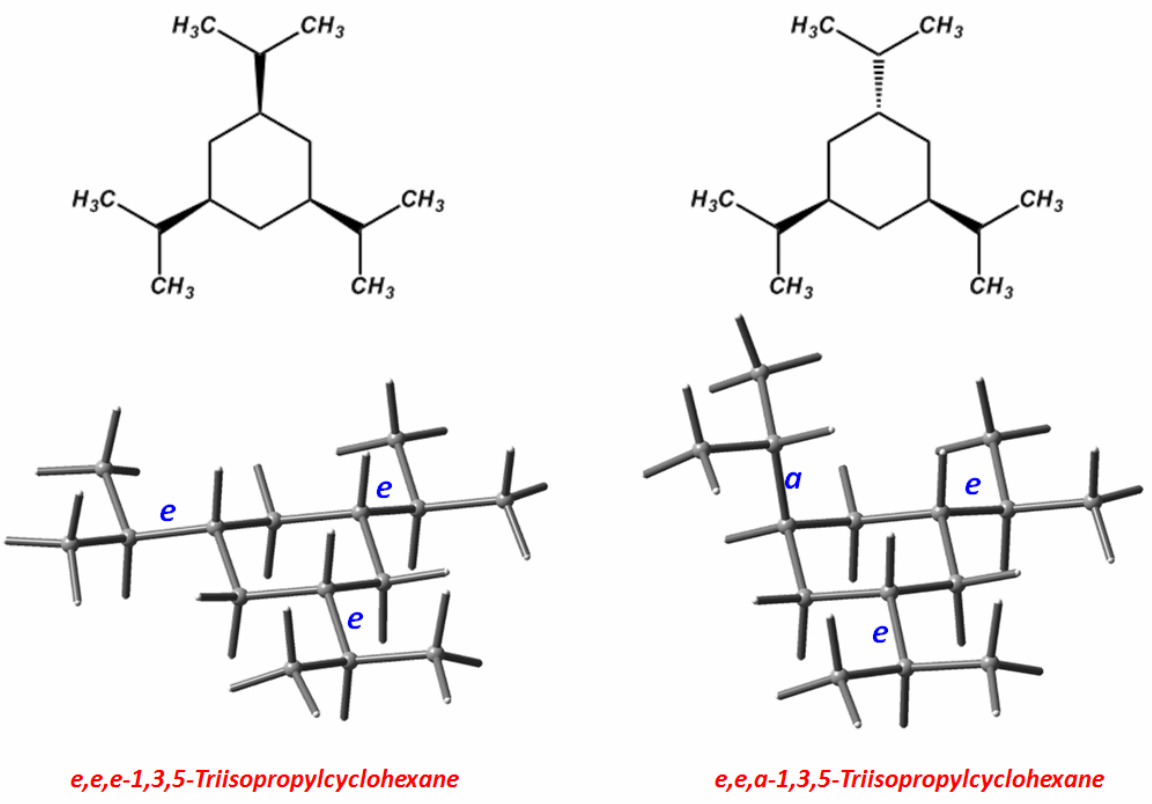


Figure 11 – The *e*,*e*,*e*-geometry and *e*,*e*,*a*-geometry isomers of 1,3,5-triisopropylcyclohexane with labels indicating *e* – equatorial or *a*-axial location of the substituent on the cyclohexane ring (shown here as three-dimensional representations).

Quantitative analysis was performed for samples synthesized by both Eastern Sources Inc. and Sigma-Aldrich. In both cases, the averaged (based on two replicates) peak areas were about 88% for the first peak (*eee*-isomer) and 11% for the second peak (*eea*-isomer). Detailed results for the major peaks and contaminants are presented in Table 10. TIPCX synthesized by Eastern Sources was contaminated by lower boiling point material located in area A (Figure 10a) in contrast to the Sigma-Aldrich TIPCX, which was contaminated to a greater extent by peaks located in area B (Figure 10b).

Table 10 – GC×GC-FID quantitative results for TIPCX (based on 2 experiments)

Compounds	**ES (area % ± SD)**	**SA (area % ± SD)**
e,e,e-1,3,5-triisopropylcyclohexane	88.15 ± 0.02	87.54± 0.02
e,e,a-1,3,5-triisopropylcyclohexane	11.01± 0.02	11.20± 0.02
unknown A	0.75	0.28
unknown B	0.09	0.98

Perhydrophenanthrene (PHP)

In selecting palette compounds for the next generation of surrogate fuels, there was a need to include a low DCN, higher-density cycloalkane that boils between 250°C and 285°C. Moreover, GC-FIMS (field ionization mass spectroscopy) results have shown (24) that there is about 9% of polycycloparaffinic material in CFA (25) target fuel.

The selected compound, which meets all the needs for the project, was perhydrophenanthrene (aka tetradecahydrophenanthrene) presented in Figure 2. Because perhydrophenanthrene is not commercially available, it was custom synthesized (via hydrogenation of phenanthrene (Figure 12a)) by Eastern Sources (13) and Sigma-Aldrich (14). In Figure 12a the most stable stereoisomer of PHP (*trans-anti-trans*-PHP) was presented, in which all cyclohexane rings have a chair conformation. The starting material (phenanthrene) is a planar aromatic molecule. By contrast, the final product is an entirely saturated compound that can exist in many stereoisomeric conformers. The six possible stereoisomers (excluding enantiomers) for perhydrophenanthrene are presented in Figure 13 (26). Five of the PHP stereoisomers were found in the final product shipped to CanmetENERGY. Figure 12b presents the superimposed chromatograms of phenanthrene and perhydrophenthene. The reader may notice substantial shifts in both dimensions for the PHP peaks in relation to the phenanthrene peak.

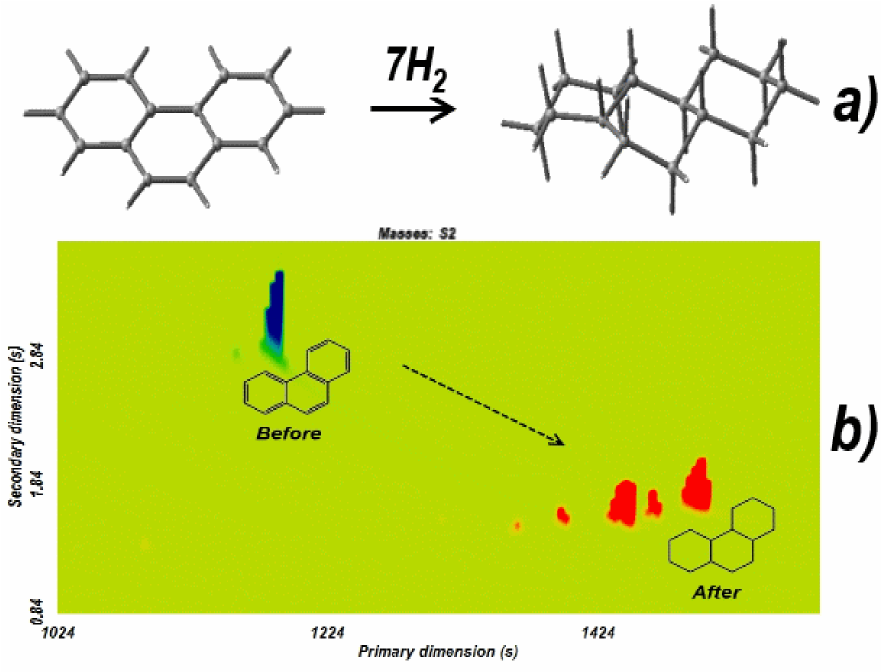


Figure 12 – (a) Schematic of the phenanthrene hydrogenation reaction. (b) The changes in the relative locations of products (stereoisomers of PHP) and substrate (phenanthrene) as seen by GC×GC technique.

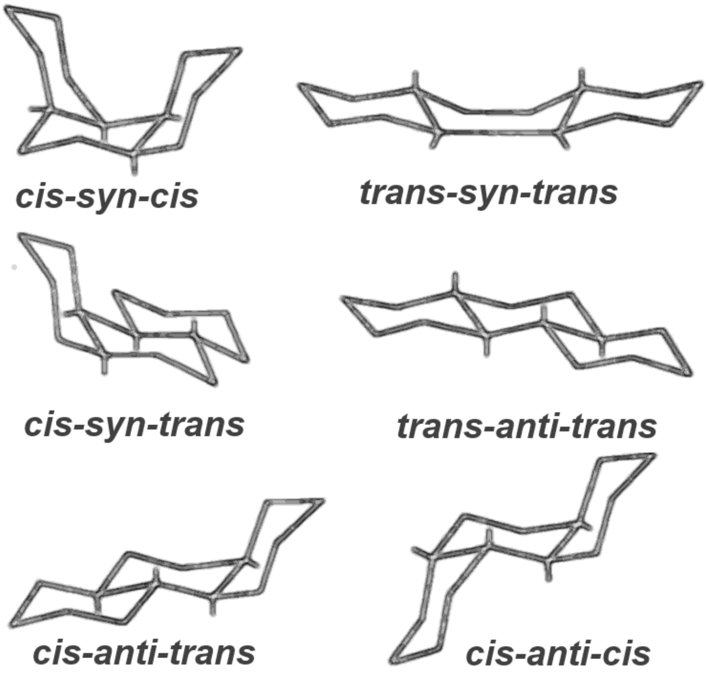


Figure 13 – Structures and configurations of perhydrophenanthrene stereoisomers (27).

PHP samples synthesized by both Eastern Sources (ES) and Sigma-Aldrich (SA) were characterized by high concentrations of the final product, constituting 99.7 wt% and 98.7 wt% of the major compound, respectively. Figure 14 presents GC×GC-FID chromatograms of the samples, showing that PHP is distributed across five of its stereoisomers (PHP A- PHP E).

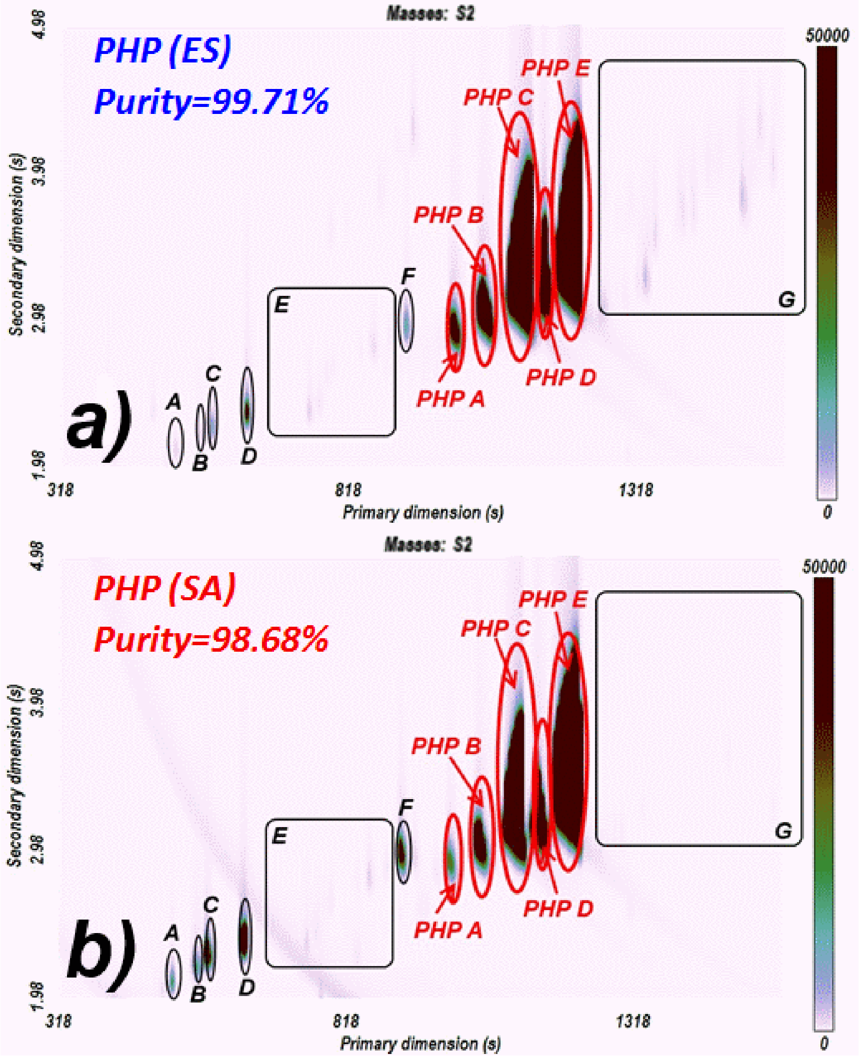


Figure 14 – GC×GC-FID chromatograms of the compounds obtained after the hydrogenation reaction of phenanthrene to perhydrophenanthrene from two commercial laboratories: Eastern Sources (a) and Sigma-Aldrich (b).

There is a noticeable difference in the concentrations of the five PHP isomers (PHP A – PHP E) obtained from the two suppliers (see Figure 15a). Two of them, namely PHP C and PHP E, constitute more than 90% of the total product generated during hydrotreating. The results presented in Figure 15a show that PHP C and PHP E share the same concentration in the product obtained by ES. In the SA case, the PHP E content is almost three times that of PHP C. The different concentration distributions for the PHP isomers may be evidence of different hydrogenation conditions used by SA and ES during PHP synthesis. A short discussion on the influence of reaction conditions on the reduction of phenanthrene has been previously reported in (24). The most probable compound structures associated with the major contaminants (based on MS NIST searching procedure) are presented in Appendix B (Figure B1).

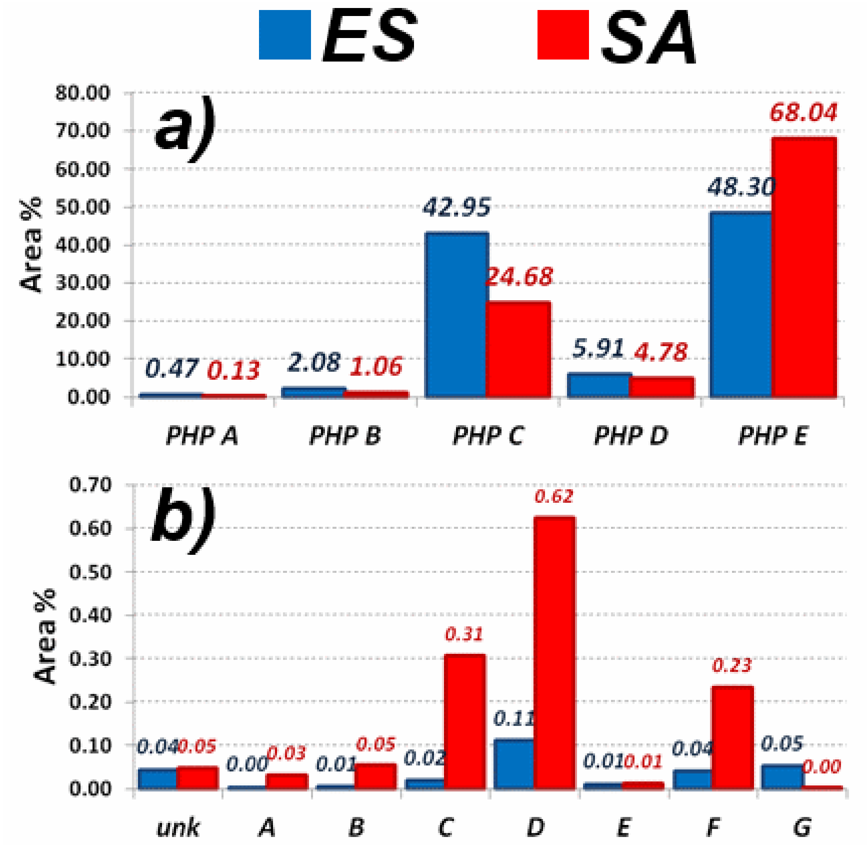


Figure 15 – GC×GC-FID quantitative results for five PHP stereoisomers (a) and impurities (b)

In order to relate PHP structures (from Figure 13) with particular PHP peaks found in the GC×GC chromatograms, a GC×GC-TOFMS experiment was performed on the samples. The resulting mass spectra of stereoisomers of PHP are presented in Figure16. Unfortunately, the mass spectra of all five PHP isomers are indistinguishable (qualitatively identical) which resulted in an inability to assign a structure to a GC×GC peak.

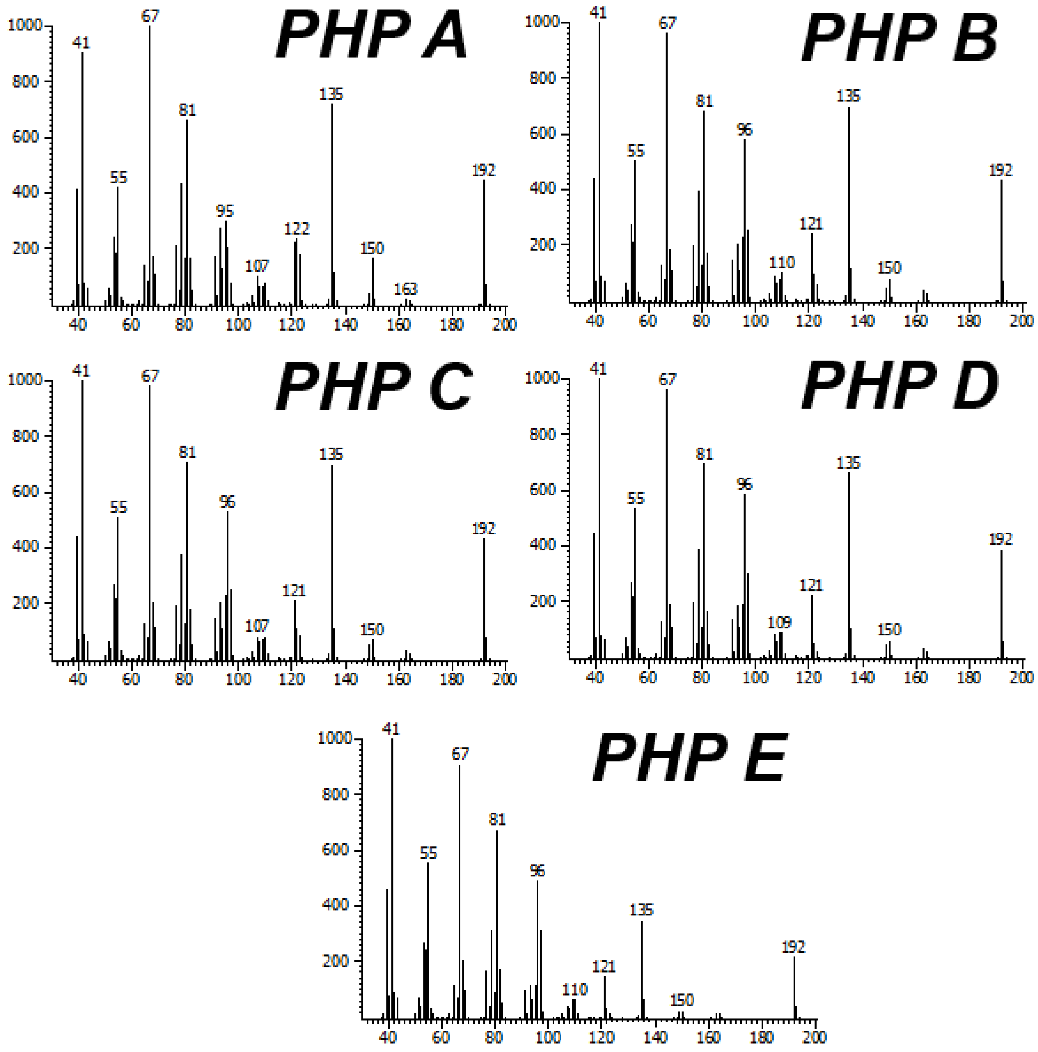


Figure 16 – MS of the PHP stereoisomers found in one of the samples

As previously mentioned, PHP is not commercially available. As a result, most of the physical properties for this compound are unknown. Several properties can be calculated using group contribution methods (28) or predicted by using QSPR (quantitative structure-property relationship) (29) analysis (as shown in Table 11). The values presented in Table 11 will be reevaluated when necessary. The boiling point (bp), reported in the table, was calculated based on the group contribution method available on *www.chemspider.com*. This calculated value can be indirectly confirmed by the well-known relation between boiling points and GC-retention time for hydrocarbons (30). The simple mathematical conversion of the primary GC×GC retention times of five PHPs to the boiling point values resulted in the bp range of 266-276°C.

Table 11 – Perhydrophenanthrene – measured and calculated values of selected physical properties.

Cetane Number	30 a) and 38.8±1.0 b)
Flash Point	105.1±11.7 °C c)
Boiling Point	273.7±7.0 °C c)
Index of Refraction	1.488 c)
Density	0.9±0.1 g/cm^3 c)
Surface Tension	31.4±3.0 dyne/cm c)

a) Predicted by QSPR in (31),

b) DCN value as measured by Matt Ratcliff from National Renewable Energy Laboratory (NREL),

c) Calculated using: *www.chemspider.com*

In this section, it was shown that PHP samples are composed of five stereoisomers. Therefore, the value of a given measured physical property for the mixture will not necessarily be representative of any individual stereoisomer. The example of two isomers of decalin presented earlier (see Section 4.1.3 – Table 8) shows that physical properties can be strongly dependent on the spatial structure of the particular stereoisomer. The comparison of the cetane numbers of the two decalin isomers shows how different the kinetic behavior can be as well (19).

4.1.4 NAPHTHENO-AROMATICS

Tetralin (TET)

Tetralin (1,2,3,4-tetrahydronaphthalene) is the simplest naphtheno-aromatic found in jet and diesel fuels. TET is the only naphthoaromatic compound (i.e., compound with one or more naphthenic and one or more aromatic rings) selected and investigated for use as a blending component for surrogate diesel fuels. This compound is used in combustion studies because of its low price and availability in relatively pure form. Its chemical kinetic mechanism observed during combustion was recently measured (32, 33). The 3D structure of TET is presented in Figure 3. It can be observed that one of the rings is aromatic and flat, which may affect the combustion properties of this molecule (31).

The tetralin sample provided to CanmetENERGY appeared to be a high purity compound, exceeding the purity stated by the manufacturer (see Table 3). Figure 17 presents its

GC×GC-FID chromatogram. Two of the four major impurities, *cis*-decalin and naphthalene, accounted for 0.5% of the total area. Detailed speciation of impurities in the tetralin sample is included in Table 12.

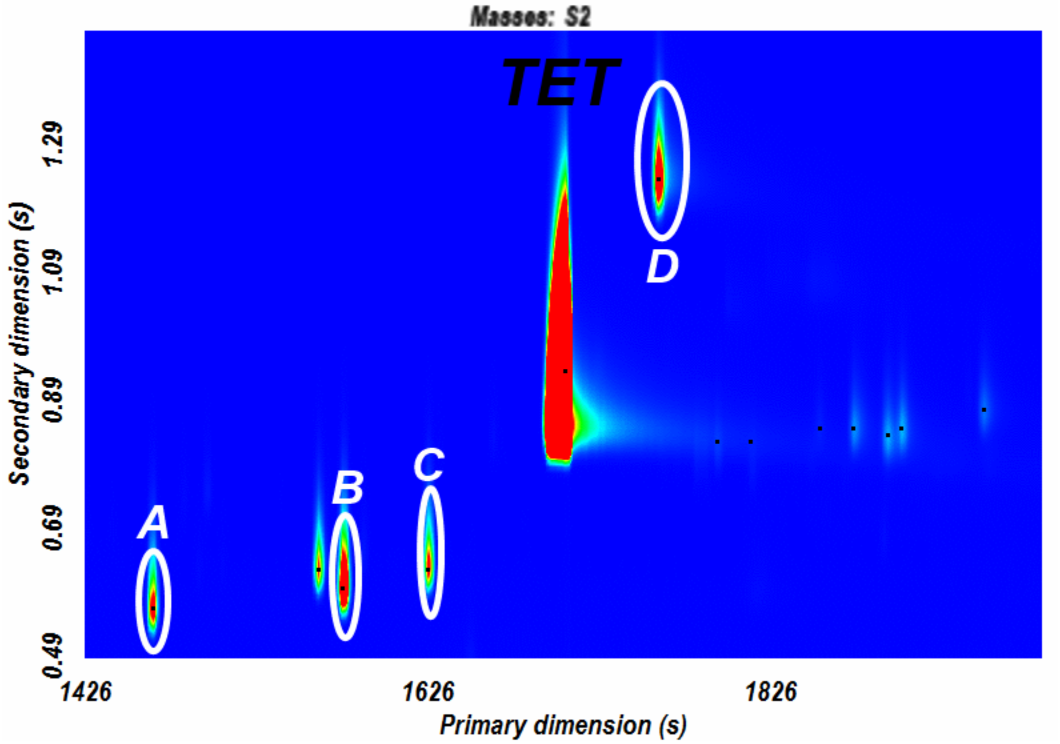


Figure 17 – GC×GC-FID chromatogram of tetralin

Table 12 – GC×GC-FID quantitative results for normal tetralin (based on three experiments)

ID	**Major compound name (area% ± SD)**	**Contaminations (area%)**
TET	tetralin (99.23 ± 0.02)	(A) *trans*-decalin (0.1); (B) *cis*-decalin (0.23); (C) 1-cyclopentylcyclopentane (0.09); (D) naphthalene (0.25) unknown (0.09)

4.1.5 AROMATICS

1,2,4-trimethylbenzene (TMB)

1,2,4-trimethylbenzene is one of the least expensive representatives of alkylbenzenes in diesel and jet fuels. The GC×GC chromatogram of TMB is presented in Figure 18 where two isomers of trimethylbenzene (comprising ~0.4 %) are the major contaminants in the sample. The other impurity (compound C in Figure 18) was identified as cycloparaffinic. Using only one-dimensional (1D) separation, it is expected that compound C may co-elute with TMB because of the same retention time on the primary column. Quantitative results are presented in Table 13.

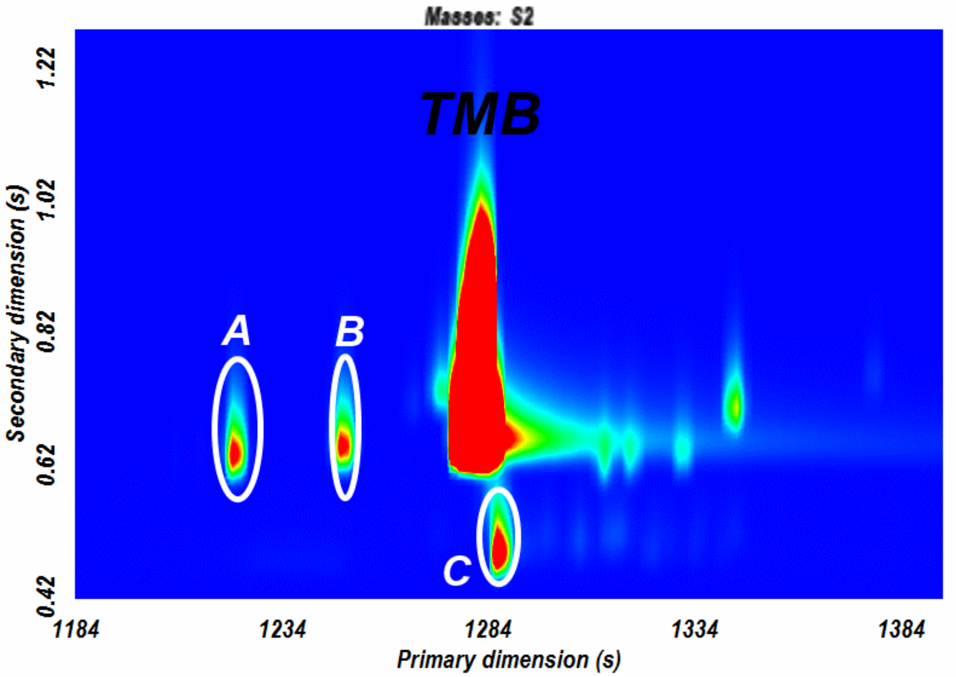


Figure 18 – GC×GC-FID chromatogram of 1,2,4-trimethylbenzene.

Table 13 – GC×GC-FID quantitative results for 1,2,4-trimethylbenzene (based on three experiments)

ID	Major compound name (area% ± SD)	Contaminations (area%)
TMB	1,2,4-trimethylbenzene (99.25 ± 0.02)	(A) isomer of trimethylbenzene (0.22); (B) isomer of trimethylbenzene (0.21); (C) cycloparaffin (0.18); unknown (0.34)

1,3,5-triisopropylbenzene (TIPB)

In contrast with TMB, the next aromatic representative has a more complex structure and is more expensive. Triisopropylbenzene was added to the surrogate palette because it is characteristic of the multi-substituted, low cetane and larger monoaromatics found in commercial diesel fuels (15). The purity of commercial TIPB can be as low as 95 wt%. In order to acquire TIPB with at least 98 wt% purity, custom synthesis was required. Figure 19 presents the GC×GC chromatogram of the TIPB product where a significant portion of contamination is ascribed to one peak (peak B in the figure). Peak B was identified as 1,2,4-triisopropyl benzene (based on mass spectra and a NIST library search). The exact identity of the remaining impurities (peaks A and C) is unknown; based on mass spectra they may be classified as isomers of C9-alkylbenzene.

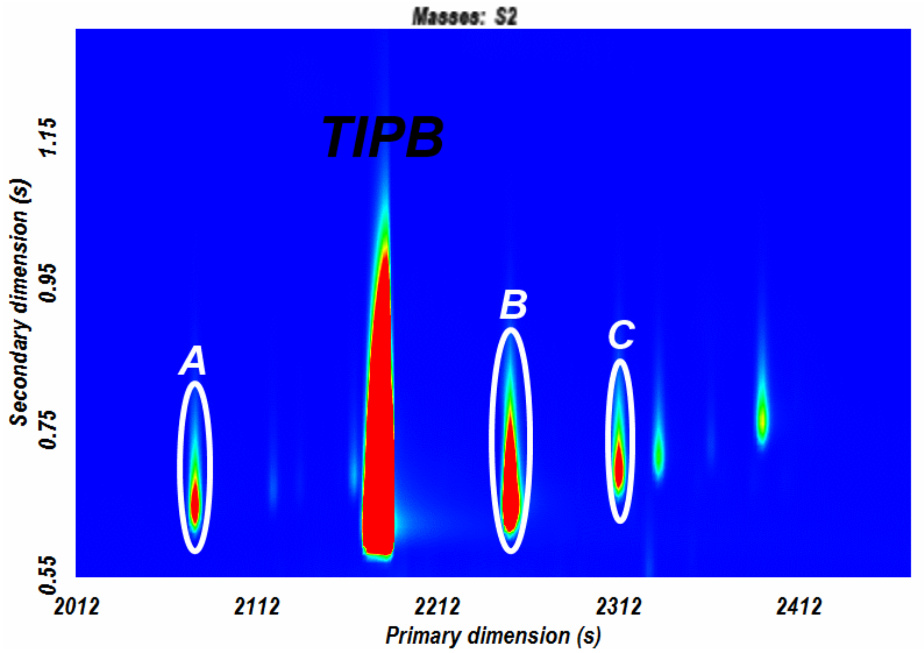


Figure 19 – GC×GC-FID chromatogram of 1,3,5-triisopropylbenzene

Table 14 – GC×GC-FID quantitative results for 1,3,5-triisopropylbenzene (based on three experiments)

ID	Major compound name (area% ± SD)	Contaminations (area%)
TIPB	1,3,5-triisopropylbenzene (98.11 ± 0.02)	(A) C9-alkylbenzene (0.18); (B) 1,2,4-triisopropylbenzene (1.27); (C) C9-alkylbenzene (0.20); unknown (0.24)

1-methylnaphthalene (1MN)

In the ground-vehicle industry, 1-methylnaphthalene has been used for many years as a hydrocarbon reference standard for determination of ignition quality of diesel fuels. Historically the cetane number (CN) of 1-methylnaphthalene (1MN) was assigned as 0. However, due to its carcinogenic side effects (34), 1-methylnaphthalene was substituted by 2,2,4,4,6,8,8-heptamethylnonane (isocetane) with a CN of 15 (35). 1MN is still widely used in many engine research studies, mostly as a blending component of surrogate fuels (36).

We found previously that commercially available 1MN (5, 9) had a purity of 95.5%, with methylbenzothiophene as the major contaminant. Therefore, after blending all selected compounds, we observed a high level of sulfur (>400 ppm) in the final surrogate fuel (5). This did not meet the ultra-low-sulfur fuel criterion, disqualifying it as a diesel fuel component for testing. Recently, in another study, it was found that a commercially available 1MN standard with stated purity >99% (as reported by manufacturer) contained up to 1.3 wt% sulfur and 0.2 wt% nitrogen (37). Further study showed that methylbenzothiophene and methylindole were major contaminants of the 1MN standard.

Since 2012, participants of the AVFL-18a project sought sulfur-free sources of 1MN without success. All collected standards (even those claimed by the supplier to be sulfur-free) were contaminated by methylbenzothiophene in the range of 500 - 10,000 ppm S. This may be because 1MN is frequently produced from coal tar by first extracting the compounds containing heteroatoms and phenols, then filtering off the crystallized 2-methylnaphthalene and redistilling the filtrate to yield 1MN (38). Methylbenzothiophene and 1MN coexist in nature. Moreover, they have very similar physical properties which make them almost impossible to separate from natural sources using conventional techniques.

Attempts at chemical purification of the 1MN such as desulfurization with sodium or hydrogenation did not provide the desired results. Overall, approximately a dozen purification and custom-synthesis approaches were explored to achieve a 1MN sample with the desired specifications (i.e., high purity (>98%) and low sulfur content (<15 ppm)). Finally, the AVFL-18a Panel attempted to obtain high-purity, low sulfur 1MN by custom synthesis at Eastern Sources. Two subsamples of newly synthesized 1MN from two different batches were provided to estimate purity. Results are presented in Figure 20 and Figure 21. The top row of Figure 20 shows chromatograms of the 1MN sample from the first batch. The bottom row shows chromatograms of samples from the second batch. It is clearly evident that the second batch is more contaminated by side products of the 1MN synthesis than the first batch. Therefore, the estimated purities for these two batches are distinctly different, equal to 96% and 88% for the first batch and second batch, respectively. The samples differ not only quantitatively, but also qualitatively. In Figure 20 white ovals indicate peaks which are common for both samples, whereas peaks marked by black ovals show important differences between the first and second batches.

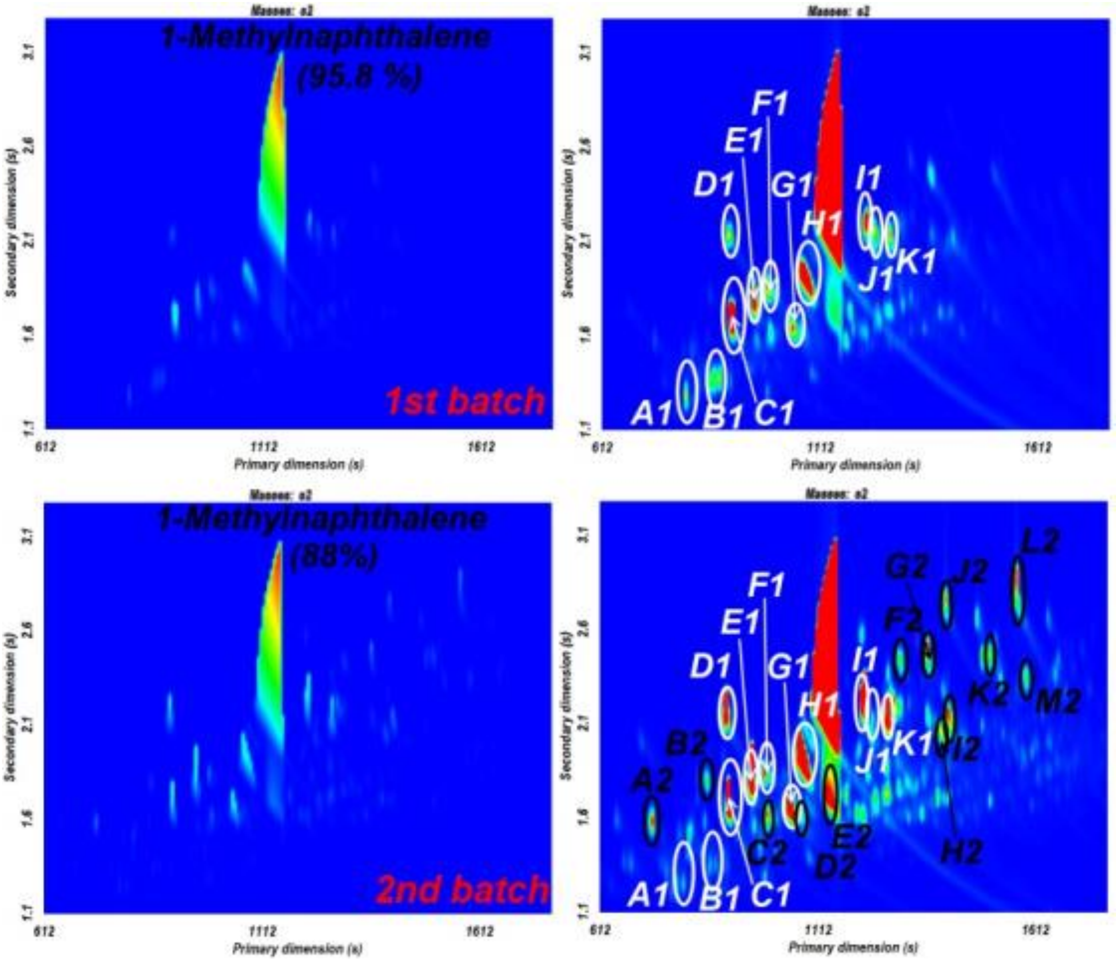


Figure 20 – GC×GC-FID chromatograms of 1-methylnaphthalene: first batch (upper figures) and second batch (bottom figures). The chromatograms on the right panel are re-plotted after applying the color intensity enhancement procedure on chromatograms located in the left panel.

In the first batch ~30 well-resolved peaks were found to account for about 4% contamination. For the second batch, the number of peaks was at least double. Most of the compounds had concentrations much lower than 0.001 wt%. Figure 21 presents a quantitative comparison between batches of contaminants. The major contaminants in the first batch of 1MN were C1 (1-ethyl-2,3-dihydro-1H-indene), H1 (5-methyltetralin), and E1 (1-methyltetralin). For the second batch the most abundant peaks were H1, E1, I1 (biphenyl), C1, G1 ((3-methylcyclopentyl) benzene), D1 (naphthalene), K1 (dimethylnaphthalene), and E2 (cyclohexylbenzene). Appendix C presents more details such as digitized data, structures, and mass spectra of contaminants in Table C1 and Figure C1, respectively.

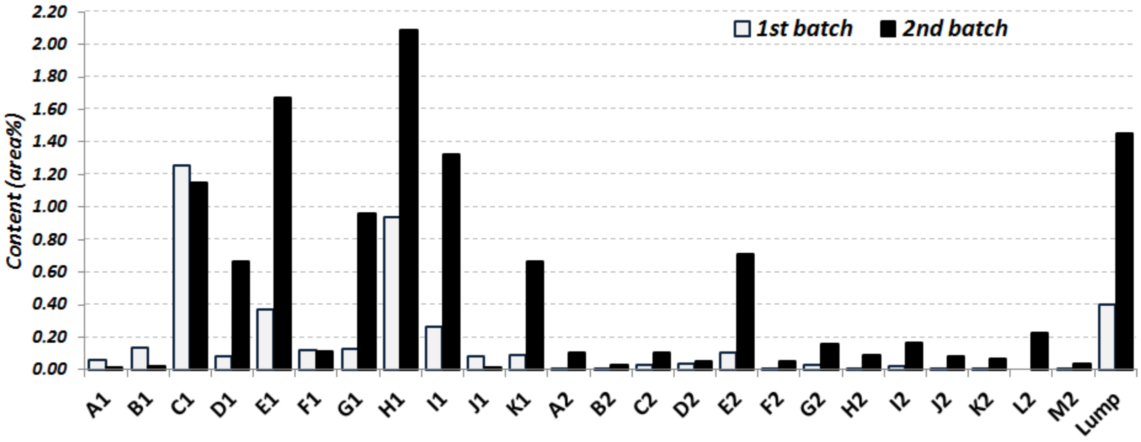


Figure 21 – Bar plot showing contamination levels based on the GC×GC-FID experiment for 1MN samples: first batch (white bars) and second batch (black bars).

With regard to sulfur, Figure 22 presents GC×GC-SCD results for both first and second batches. In the SCD chromatograms, no peaks were observed (besides the noise), which indicates a very low level of sulfur (< 1ppm) for these samples.

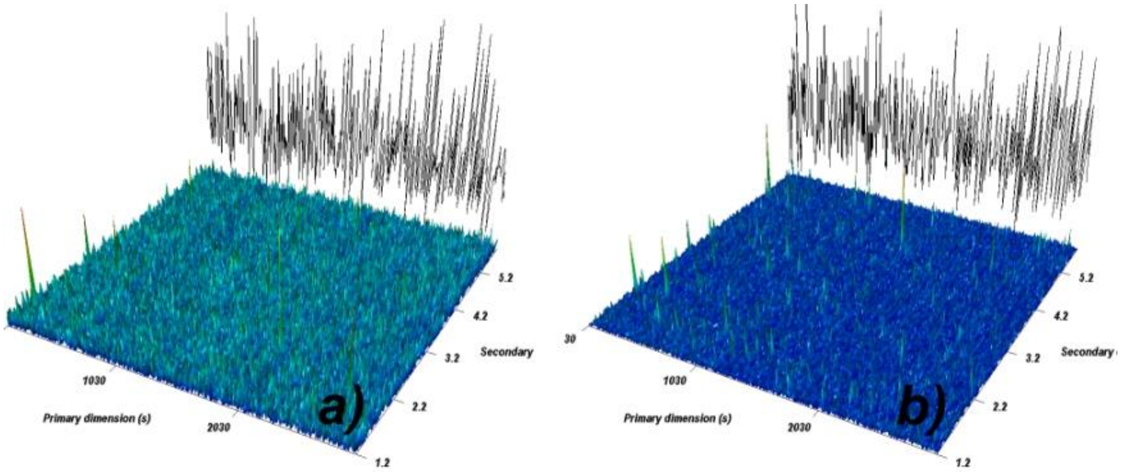


Figure 22 – GC×GC-SCD chromatograms of 1-methylnaphthalene: first batch (a) and second batch (b)

For the above samples only one of the two desired specs (low sulfur) was met. The other, low impurity level, was not achieved. Therefore, an additional purification of 1MN was performed and the resulting 1MN sample was shipped to CanmetENERGY and analyzed by GC×GC-FID for determination of its purity. This 1MN appears to be a highly pure compound, with purity exceeding 99 wt%. Figure 23a presents the GC×GC-FID chromatogram of 1MN with only one major contaminant compound. Quantitative results of impurity level in 1MN are shown in Table 15. In addition to high purity, 1MN is characterized by a 'sulfur free' profile as seen in Figure 23b.

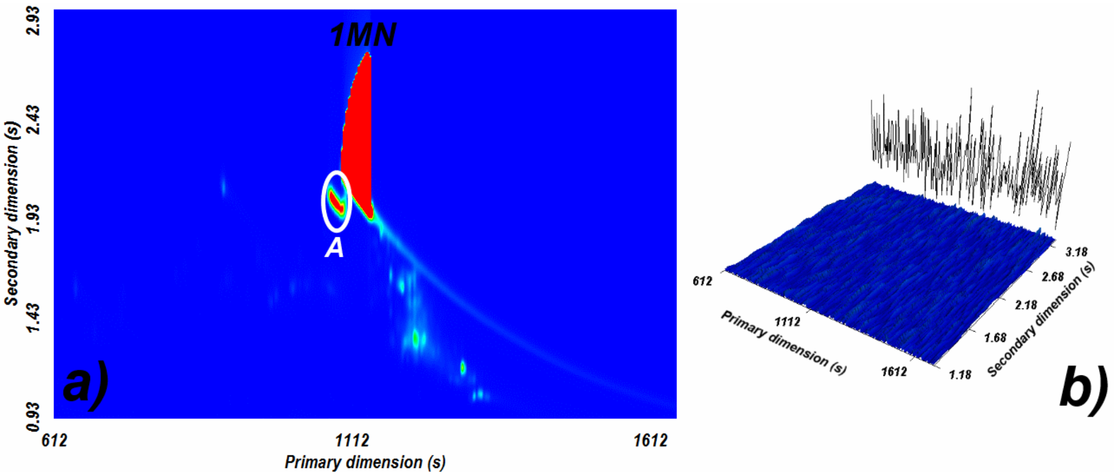


Figure 23 – GC×GC chromatograms of 1-methylnaphthalene synthesized by Eastern Sources: the FID profile (a), the SCD profile (b)

Table 15 – GC×GC-FID quantitative results for 1-methylnaphthalene (based on three experiments)

ID	Major compound name (area% ± SD)	Contaminations (area%)
1MN	1-methylnaphthalene (99.50 ± 0.02)	(A) 5-methyl-tetralin (0.28); unknown (0.22)

4.2 SURROGATE FUELS

The overall goal of the AVFL-18a project was to prepare and measure the selected physical and chemical properties of high purity, ultralow-sulfur surrogate diesel fuel blends. To accomplish this task, four diesel surrogates of different compositional-complexity were blended from the surrogate palette compounds described and investigated in the previous sections. Two lower-compositional-complexity (V0a, V0b) and two higher-compositional-complexity (V1, V2) blends were formulated (3).

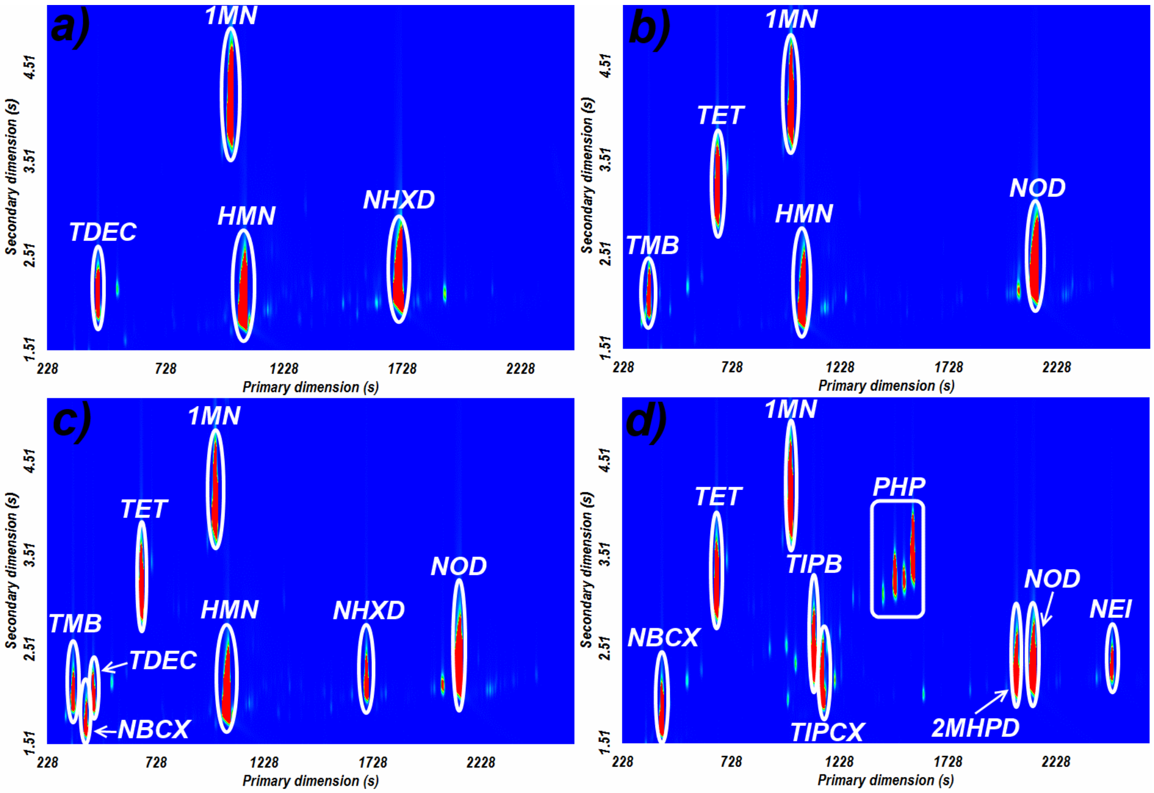


Figure 24 – GC×GC-FID chromatograms of surrogate fuel samples: V0a (a), V0b (b), V1 (c), V2 (d)

After blending by Chevron, the four surrogate diesel fuels were submitted to CanmetENERGY for GC×GC-FID analysis to confirm the target concentrations of palette compounds in the blends (see Figure 24). The surrogate fuel compositions determined by the GC×GC technique are provided in Table 16. For comparison purposes, the target concentrations of palette compounds are also included in Table 16. In general, there is excellent agreement between concentrations reported by the lab where the surrogate blends were prepared and the results obtained by GC×GC-FID. The observed differences may be explained by the fact that the impurity of the surrogate palette compounds was not taken into consideration during blending steps, as well as the uncertainties associated with an electronic balance (δ=0.1g).

Table 16 – Surrogate fuels composition.

	V0a (4-components)		**V0b (5-components)**		**V1 (8-components)**		**V2 (9-components)**	
	Lab. blend (wt%)[a)]	**GC×GC (wt%)[b)]**	**Lab. blend (wt%)**	**GC×GC (wt%)**	**Lab. blend (wt%)**	**GC×GC (wt%)**	**Lab. blend (wt%)**	**GC×GC (wt%)**
NHXD	32.20	32.02	0	0	3.20	3.23	0	0
NOD	0	0	32.10	31.91	27.30	27.13	15.20	15.22
NEI	0	0	0	0	0	0	1.20	1.24
HMN	42.00	41.79	32.80	32.61	35.10	35.05	0	0
2MHPD	0	0	0	0	0	0	10.20	10.30
NBCX	0	0	0	0	3.80	3.71	14.80	14.59
TIPCX	0	0	0	0	0	0	12.80	12.55
TDEC	10.50	10.31	0	0	4.00	3.95	0	0
PHP	0	0	0	0	0	0	6.40	6.25
TET	0	0	14.80	14.70	10.80	10.74	12.00	11.82
TMB	0	0	8.10	7.80	4.80	4.59	0	0
TIPB	0	0	0	0	0	0	16.60	16.55
1MN	15.30	15.14	12.30	12.12	10.90	10.77	10.90	10.77
impurities	N/A	0.75	N/A	0.84	N/A	0.83	N/A	0.72

[a)] Target mass % concentrations. Blends were prepared in Chevron

[b)] Measured mass % concentrations using GC×GC-FID technique (CanmetENERGY in Devon)

Figure 25 shows a “bubble plot” representation of a GC×GC-FID chromatogram of the target fuel upon which the surrogate fuels are based. The size and color of each bubble are related to compound concentration and hydrocarbon class, respectively. The procedure used for transformation of a GC×GC-FID surface plot to the ‘bubble’ representation has been described in detail elsewhere (e.g., (39)). Many different hydrocarbon types are evident in Figure 25, such as paraffins, cycloparaffins, alkylbenzenes, etc. Figure 26 depicts the palette compounds found in each surrogate overlaid on the target fuel chromatogram. This set of figures was created in order to compare the compositional complexity existing in the target diesel fuel with that observed in the diesel surrogates.

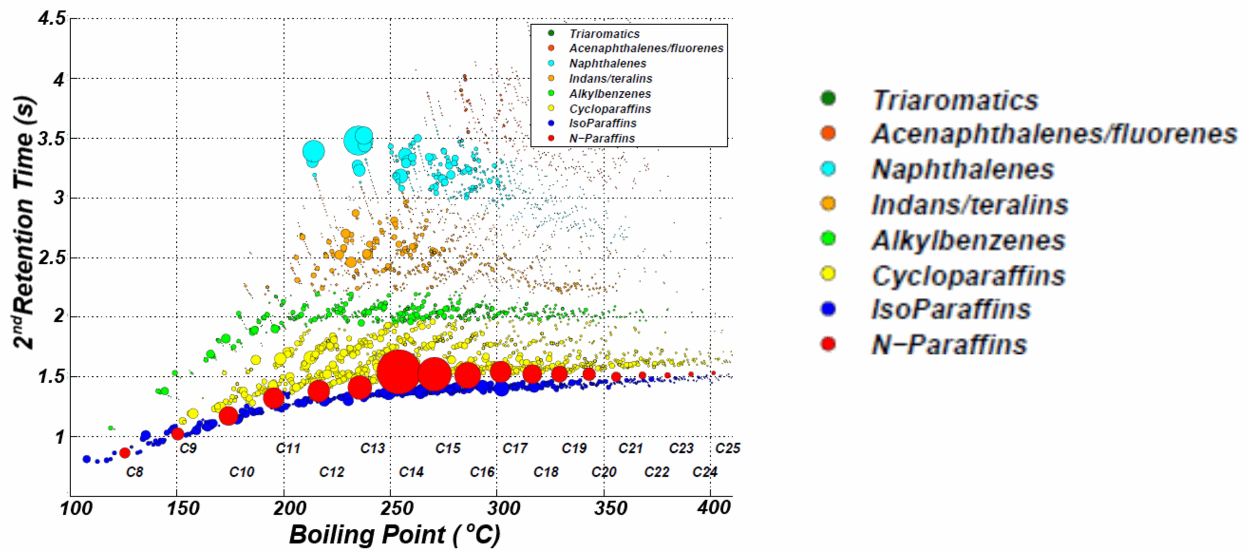


Figure 25 – GC×GC-FID chromatograms of target diesel fuel

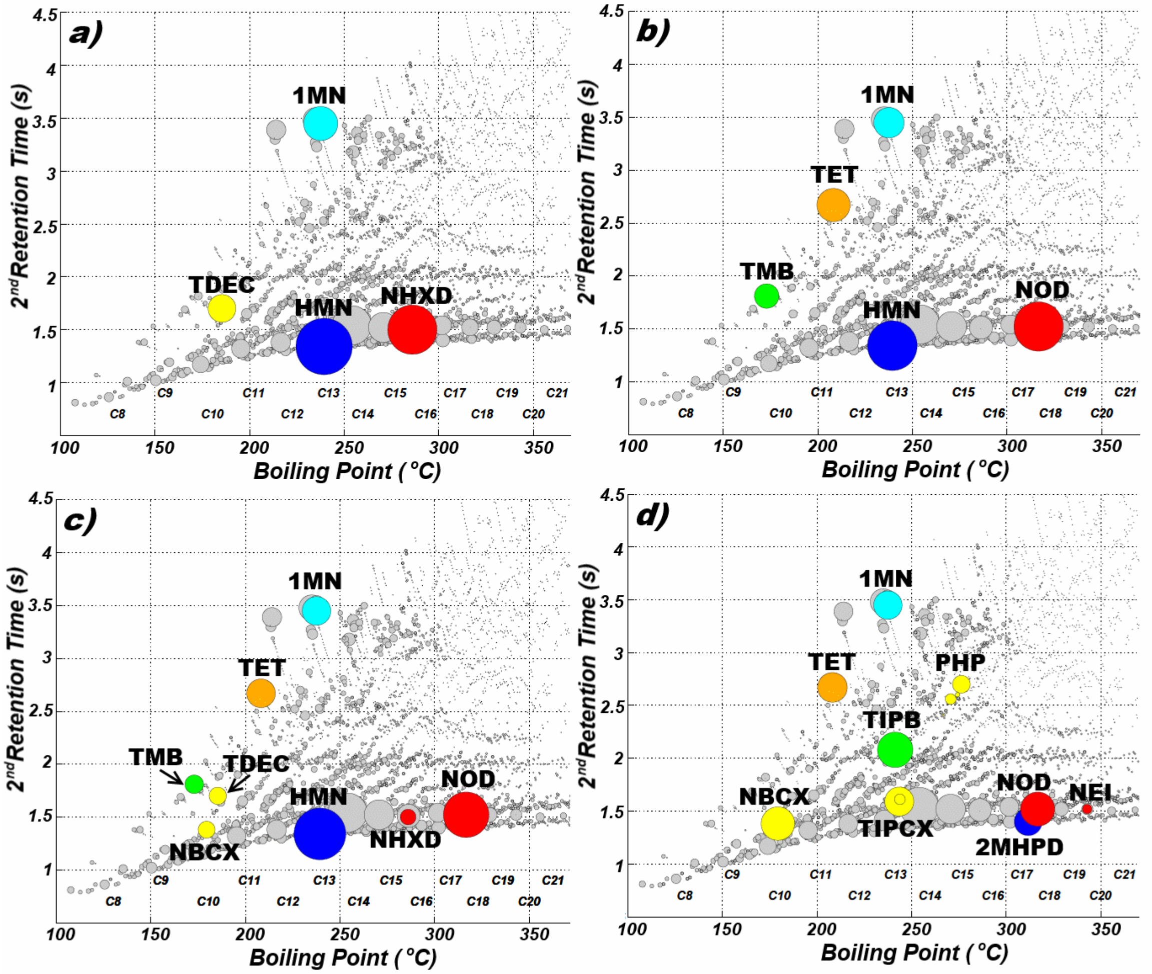


Figure 26 – GC×GC-FID chromatograms of surrogate fuels: V0a (a), V0b (b), V1 (c), V2 (d) overlaid on GC×GC chromatogram of target diesel (shown here in gray). The area and color of the bubble for each palette compound correspond to its mass fraction and hydrocarbon type, respectively.

5.0 SUMMARY AND CONCLUSIONS

Through the PERD 113 (p-001896.001) and ecoEII (p-001390.001) projects, CanmetENERGY collaborated with the US Department of Energy and the Coordinating Research Council (CRC, a non-profit organization that sponsors cooperative research among energy companies, vehicle manufacturers, and national/international labs) to develop methods for better characterization of transportation fuels and to correlate detailed fuel chemistry with physical properties and ultimately with internal combustion engine performance.

Recently, CanmetENERGY was asked by the Coordinating Research Council to estimate the purity of samples proposed for use in CRC's AVFL-18a diesel fuel surrogate blends. Such blends are being used in the development of detailed chemical kinetic models of diesel fuels and advanced combustion research in engines and combustion vessels. Comprehensive two-dimensional gas chromatography (GC×GC) with several detector types was used by CanmetENERGY to carry out these analyses.

This report documents the results of detailed analyses of the purities of 13 surrogate palette compounds involved in the preparation of the CRC AVFL-18a second generation of surrogate diesel fuels. The analytical results reported for each sample include the content of the main compound as well as detected contaminants (in weight percentage). The major conclusions of this study are:

- The palette compounds shipped to CanmetENERGY for purity analysis were generally highly pure, in a few cases exceeding 99.5 wt% (e.g. *n*-butylcyclohexane (99.8 wt%)).
- In most cases the major contaminants were identified and structures were confirmed by matching spectra with the NIST MS database.
- 1, 3, 5 – triisopropylcyclohexane consists of two stereoisomers (88 and 11 wt%, respectively).
- Five of the six perhydrophenanthrene stereoisomers were found in the final product shipped to CanmetENERGY. Two isomers constitute more than 90wt% of the total product.
- 1-methylnaphthalene synthesized by Eastern Sources appears to be a highly pure compound (>99 wt%) with virtually no sulfur content (<1 ppm).

6.0 ACKNOWLEDGEMENTS

The author would like to acknowledge financial support from the Government of Canada's interdepartmental ecoENERGY Innovation Initiative (ecoEII) and Coordinating Research Council (CRC) for the opportunity in participating and contributing to the Advanced Vehicle/Fuel/Lubricants (AVFL) committee project (AVFL-18a project). I would also like to thank Kirk Michaelian (CanmetENERGY), Chuck Mueller (Sandia National Laboratories) and the CRC AVFL-18a project members for their helpful comments and contribution the readability of this report.

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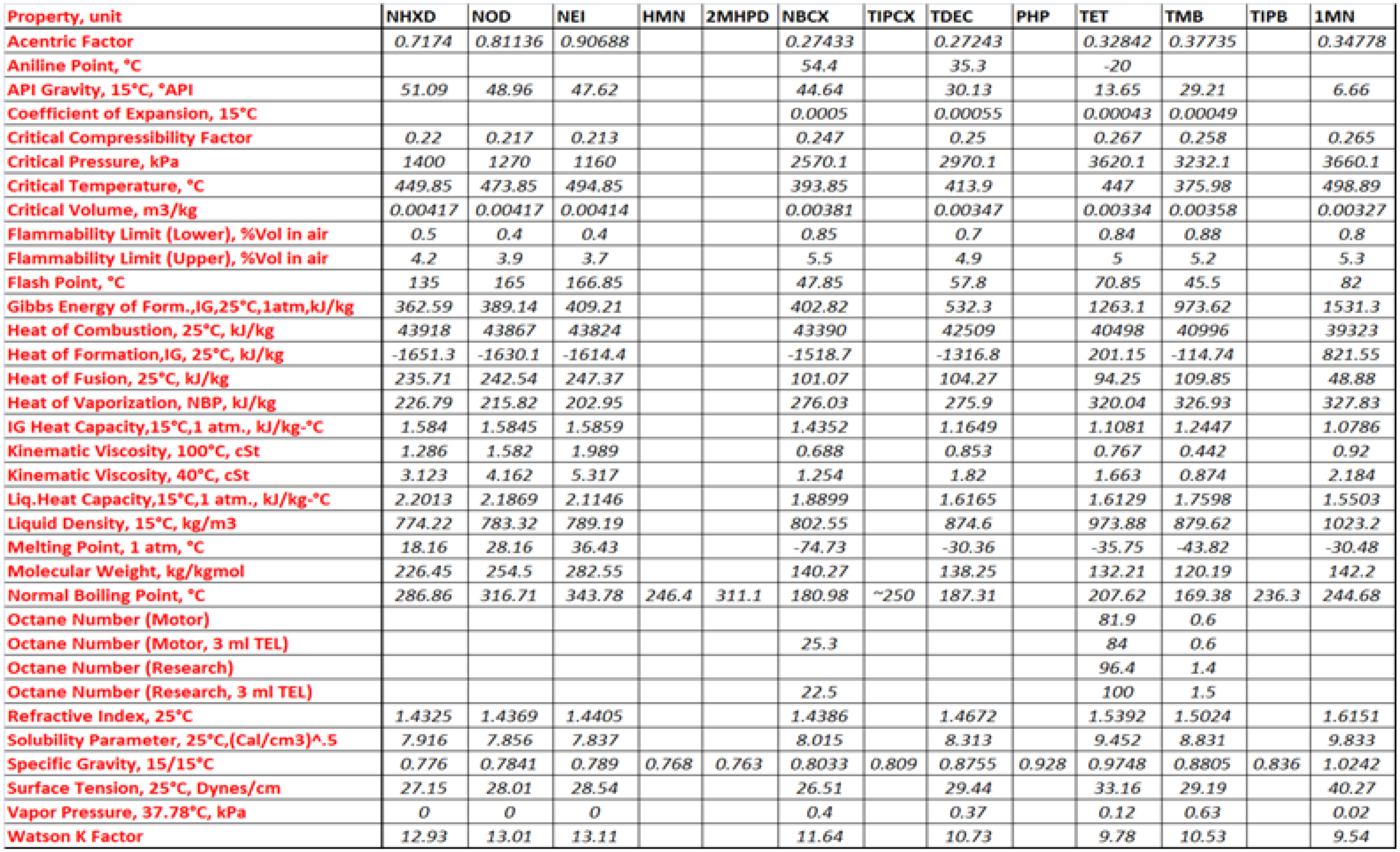
APPENDIX A: SELECTED PHYSICAL PROPERTIES OF SURROGATE PALETTE COMPOUNDS

SELECTED PHYSICAL PROPERTIES OF SURROGATE PALETTE COMPOUNDS



Property, unit	NHXD	NOD	NEI	HMN	2MHPD	NBCX	TIPCX	TDEC	PHP	TET	TMB	TIPB	1MN
Acentric Factor	0.7174	0.81136	0.90688			0.27433		0.27243		0.32842	0.37735		0.34778
Aniline Point, °C						54.4		35.3		-20			
API Gravity, 15°C, °API	51.09	48.96	47.62			44.64		30.13		13.65	29.21		6.66
Coefficient of Expansion, 15°C						0.0005		0.00055		0.00043	0.00049		
Critical Compressibility Factor	0.22	0.217	0.213			0.247		0.25		0.267	0.258		0.265
Critical Pressure, kPa	1400	1270	1160			2570.1		2970.1		3620.1	3232.1		3660.1
Critical Temperature, °C	449.85	473.85	494.85			393.85		413.9		447	375.98		498.89
Critical Volume, m3/kg	0.00417	0.00417	0.00414			0.00381		0.00347		0.00334	0.00358		0.00327
Flammability Limit (Lower), %Vol in air	0.5	0.4	0.4			0.85		0.7		0.84	0.88		0.8
Flammability Limit (Upper), %Vol in air	4.2	3.9	3.7			5.5		4.9		5	5.2		5.3
Flash Point, °C	135	165	166.85			47.85		57.8		70.85	45.5		82
Gibbs Energy of Form.,IG,25°C,1atm,kJ/kg	362.59	389.14	409.21			402.82		532.3		1263.1	973.62		1531.3
Heat of Combustion, 25°C, kJ/kg	43918	43867	43824			43390		42509		40498	40996		39323
Heat of Formation,IG, 25°C, kJ/kg	-1651.3	-1630.1	-1614.4			-1518.7		-1316.8		201.15	-114.74		821.55
Heat of Fusion, 25°C, kJ/kg	235.71	242.54	247.37			101.07		104.27		94.25	109.85		48.88
Heat of Vaporization, NBP, kJ/kg	226.79	215.82	202.95			276.03		275.9		320.04	326.93		327.83
IG Heat Capacity,15°C,1 atm., kJ/kg-°C	1.584	1.5845	1.5859			1.4352		1.1649		1.1081	1.2447		1.0786
Kinematic Viscosity, 100°C, cSt	1.286	1.582	1.989			0.688		0.853		0.767	0.442		0.92
Kinematic Viscosity, 40°C, cSt	3.123	4.162	5.317			1.254		1.82		1.663	0.874		2.184
Liq.Heat Capacity,15°C,1 atm., kJ/kg-°C	2.2013	2.1869	2.1146			1.8899		1.6165		1.6129	1.7598		1.5503
Liquid Density, 15°C, kg/m3	774.22	783.32	789.19			802.55		874.6		973.88	879.62		1023.2
Melting Point, 1 atm, °C	18.16	28.16	36.43			-74.73		-30.36		-35.75	-43.82		-30.48
Molecular Weight, kg/kgmol	226.45	254.5	282.55			140.27		138.25		132.21	120.19		142.2
Normal Boiling Point, °C	286.86	316.71	343.78	246.4	311.1	180.98	~250	187.31		207.62	169.38	236.3	244.68
Octane Number (Motor)										81.9	0.6		
Octane Number (Motor, 3 ml TEL)						25.3				84	0.6		
Octane Number (Research)										96.4	1.4		
Octane Number (Research, 3 ml TEL)						22.5				100	1.5		
Refractive Index, 25°C	1.4325	1.4369	1.4405			1.4386		1.4672		1.5392	1.5024		1.6151
Solubility Parameter, 25°C,(Cal/cm3)^.5	7.916	7.856	7.837			8.015		8.313		9.452	8.831		9.833
Specific Gravity, 15/15°C	0.776	0.7841	0.789	0.768	0.763	0.8033	0.809	0.8755	0.928	0.9748	0.8805	0.836	1.0242
Surface Tension, 25°C, Dynes/cm	27.15	28.01	28.54			26.51		29.44		33.16	29.19		40.27
Vapor Pressure, 37.78°C, kPa	0	0	0			0.4		0.37		0.12	0.63		0.02
Watson K Factor	12.93	13.01	13.11			11.64		10.73		9.78	10.53		9.54

APPENDIX B: THE MASS SPECTRA OF CONTAMINANTS FOUND IN PHP SAMPLE

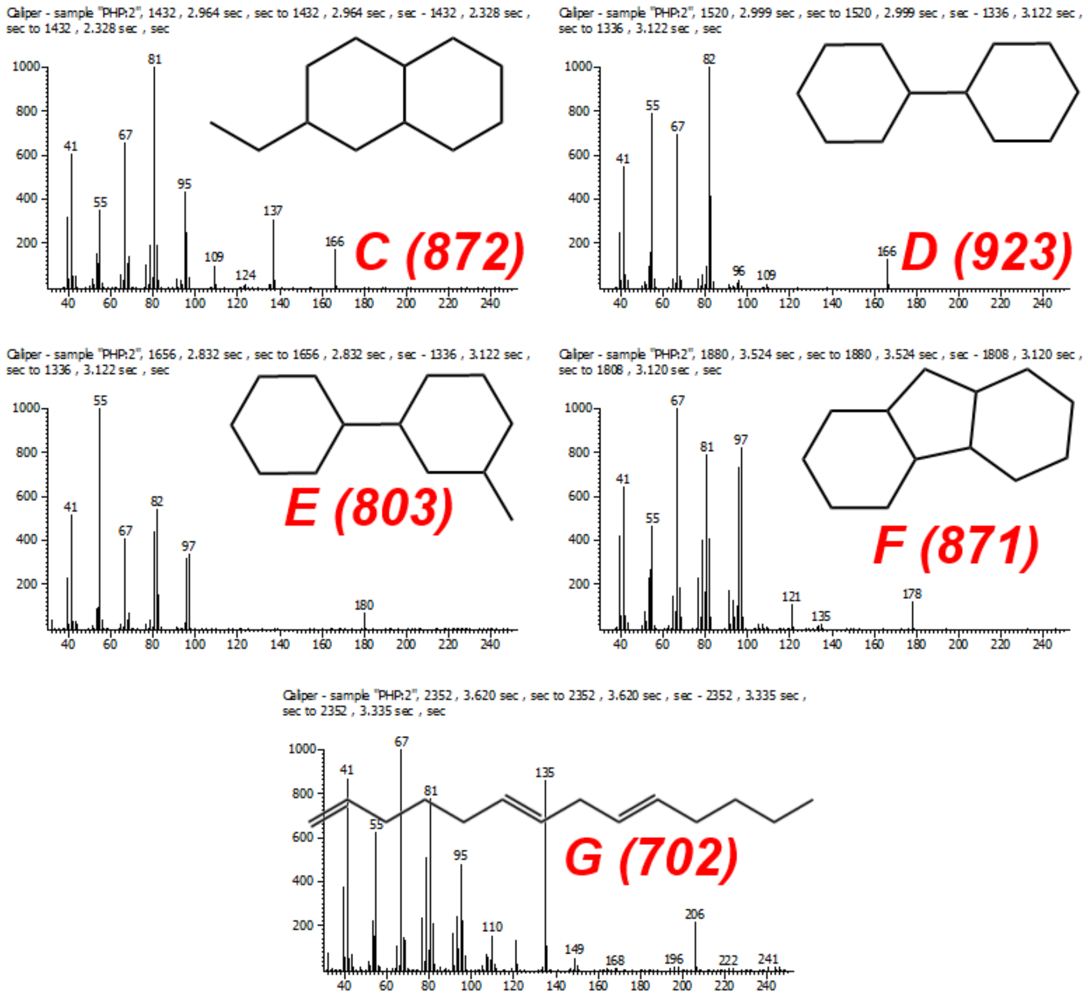
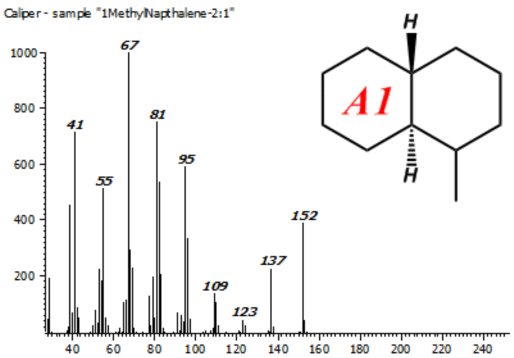


Figure B1 – The mass spectra of contaminants found in the PHP sample. Numbers in brackets represent the similarity match between experimental spectra and NIST library compound hit. The upper limit for these numbers is 999, where 999 is considered as a perfect match.

APPENDIX C: THE GC×GC-FID AND MASS SPECTRA OF CONTAMINANTS FOUND IN 1MN SAMPLE

Table C1 – GC×GC-FID quantitative results for 1-methylnaphthalene (1MN) sample (based on two experiments)

	Peak Match	1St batch		2nd batch	
Label		Content (area %)	RSD (%)	Content (area %)	RSD (%)
1MN	921	95.837	0.23	87.983	0.05
A1	891	0.058	1.15	0.012	15.27
B1	879	0.135	5.80	0.019	0.61
C1	887	1.255	1.90	1.152	0.13
D1	928	0.082	0.79	0.665	0.09
E1	922	0.370	3.64	1.672	0.10
F1	899	0.122	3.49	0.111	0.15
G1	895	0.127	26.63	0.961	0.34
H1	883	0.934	6.71	2.090	0.03
I1	915	0.267	0.32	1.324	0.15
J1	935	0.083	3.31	0.013	3.79
K1	895	0.089	6.50	0.668	0.37
A2	921	0.002	8.59	0.108	0.30
B2	924	0.001	22.13	0.032	0.42
C2	928	0.032	18.32	0.106	0.27
D2	802	0.039	56.27	0.053	0.52
E2	935	0.108	78.99	0.707	2.37
F2	890	0.000	71.78	0.048	0.52
G2	924	0.029	1.41	0.156	0.22
H2	907	0.003	18.45	0.088	0.13
I2	937	0.020	19.95	0.167	0.03
J2	NA	0.000	62.32	0.082	1.47
K2	924	0.004	43.44	0.066	0.22
L2	922	0.000	0.00	0.226	1.03
M2	890	0.000	70.27	0.039	0.58
Lump		0.403	3.02	1.452	1.12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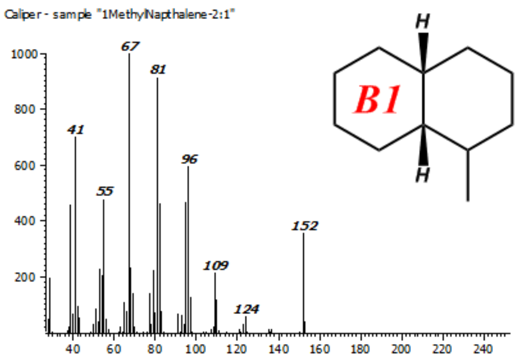
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H
H
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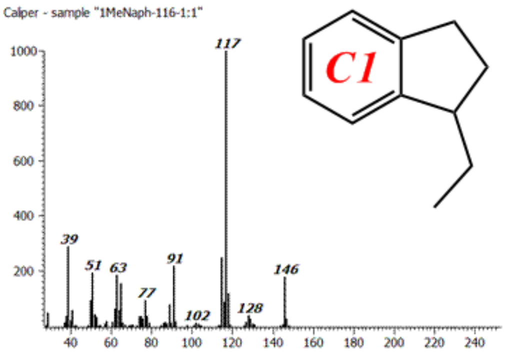
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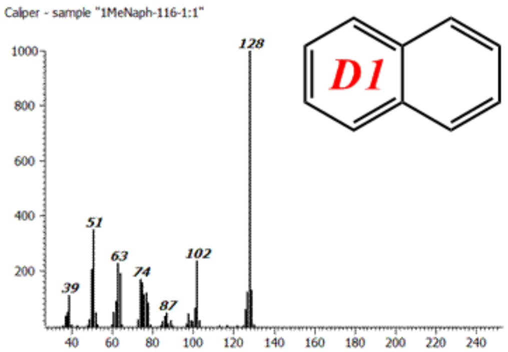
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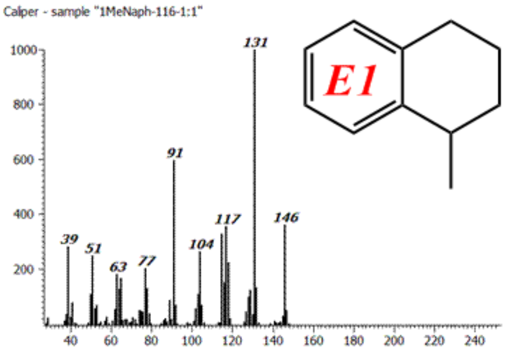
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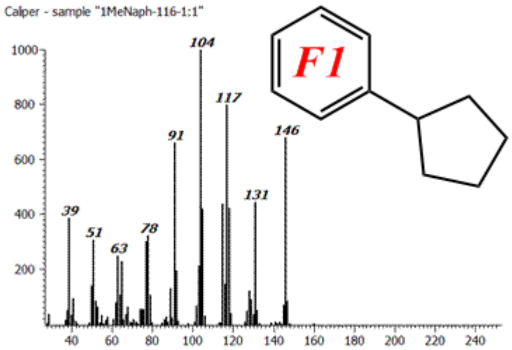
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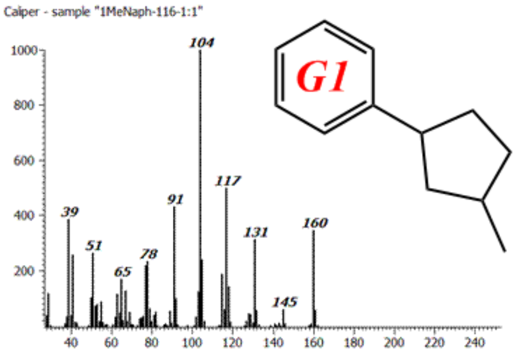
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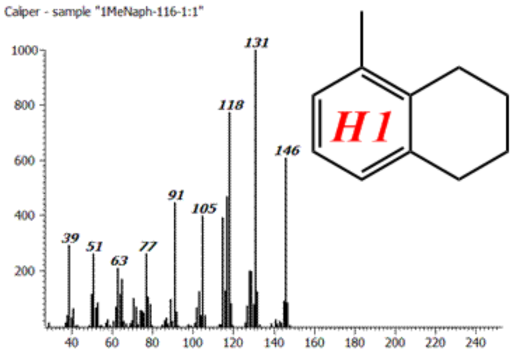
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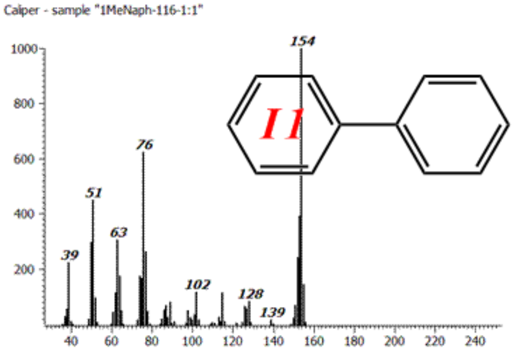
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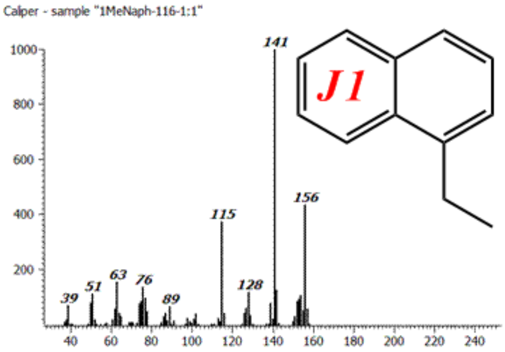
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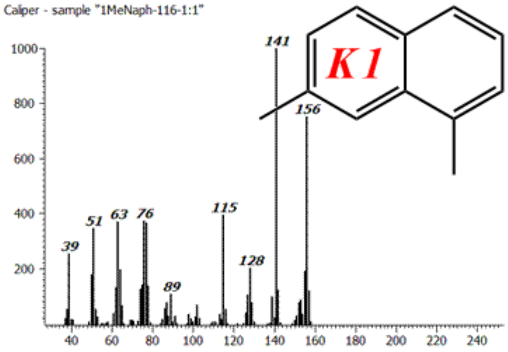
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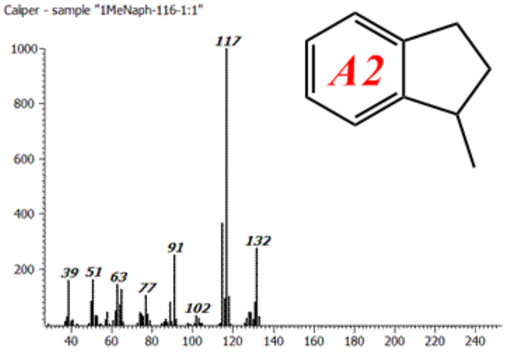
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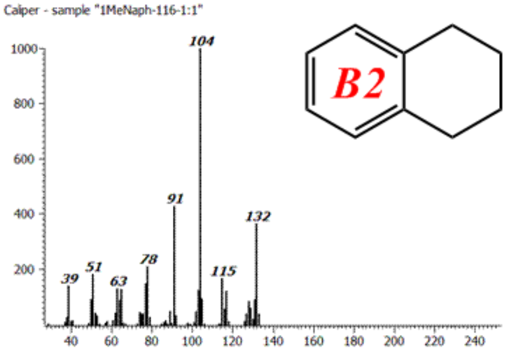
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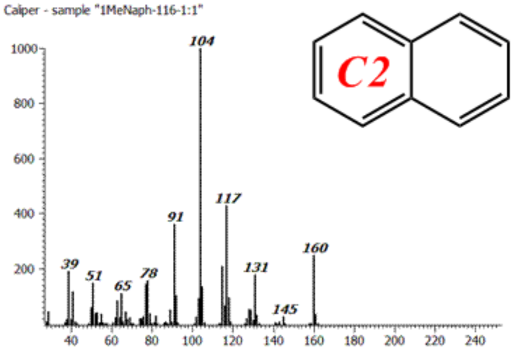
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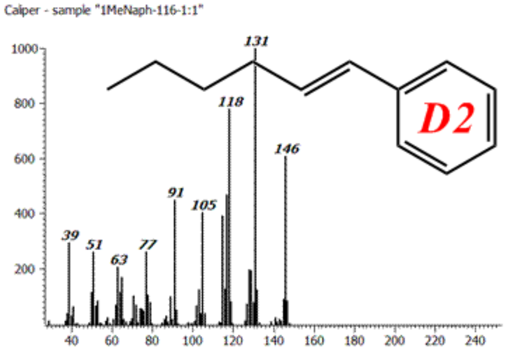
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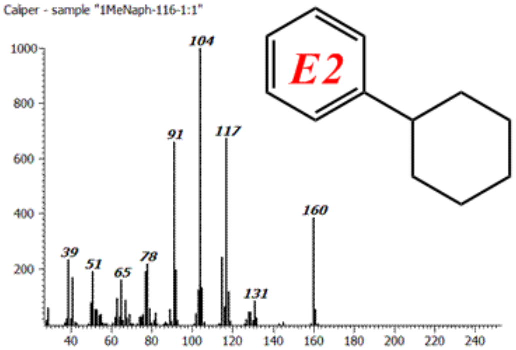
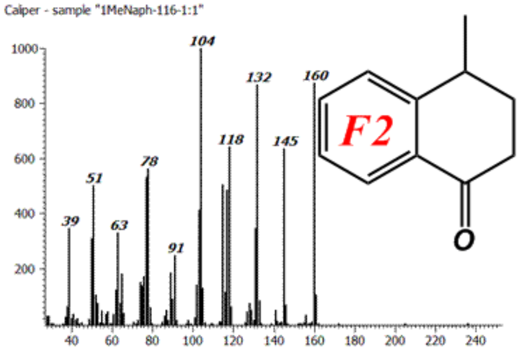
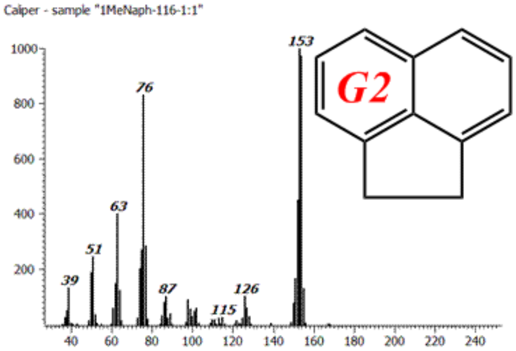
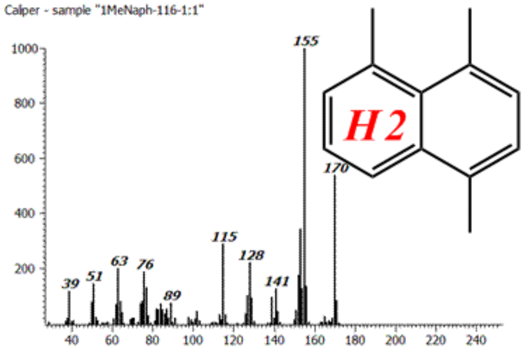
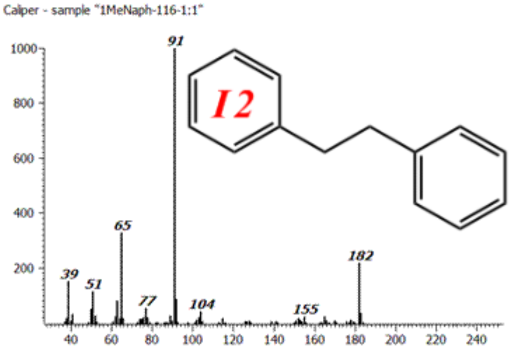
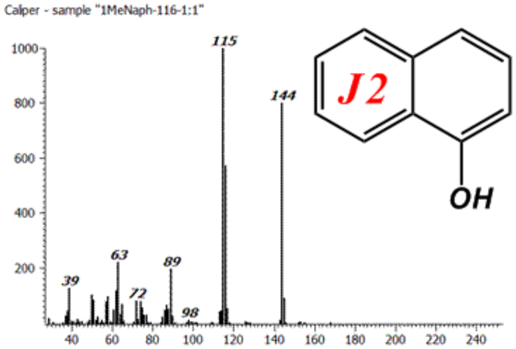

Caliper - sample "1MeNaph-116-1:1"
104
E2
91
117
160
39
51
65
78
131
1000
800
600
400
200
40
60
80
100
120
140
160
180
200
220
240


Caliper - sample "1MeNaph-116-1:1"
104
132
160
F2
118
145
78
51
39
63
91
O
1000
800
600
400
200
40
60
80
100
120
140
160
180
200
220
240


Caliper - sample "1MeNaph-116-1:1"
153
G2
76
63
51
39
87
126
115
1000
800
600
400
200
40
60
80
100
120
140
160
180
200
220
240


Caliper - sample "1MeNaph-116-1:1"
155
H2
170
115
128
63
76
39
51
141
89
1000
800
600
400
200
40
60
80
100
120
140
160
180
200
220
240


Caliper - sample "1MeNaph-116-1:1"
91
I2
65
182
39
51
77
104
155
1000
800
600
400
200
40
60
80
100
120
140
160
180
200
220
240


Caliper - sample "1MeNaph-116-1:1"
115
J2
144
OH
63
89
39
72
98
1000
800
600
400
200
40
60
80
100
120
140
160
180
200
220
240

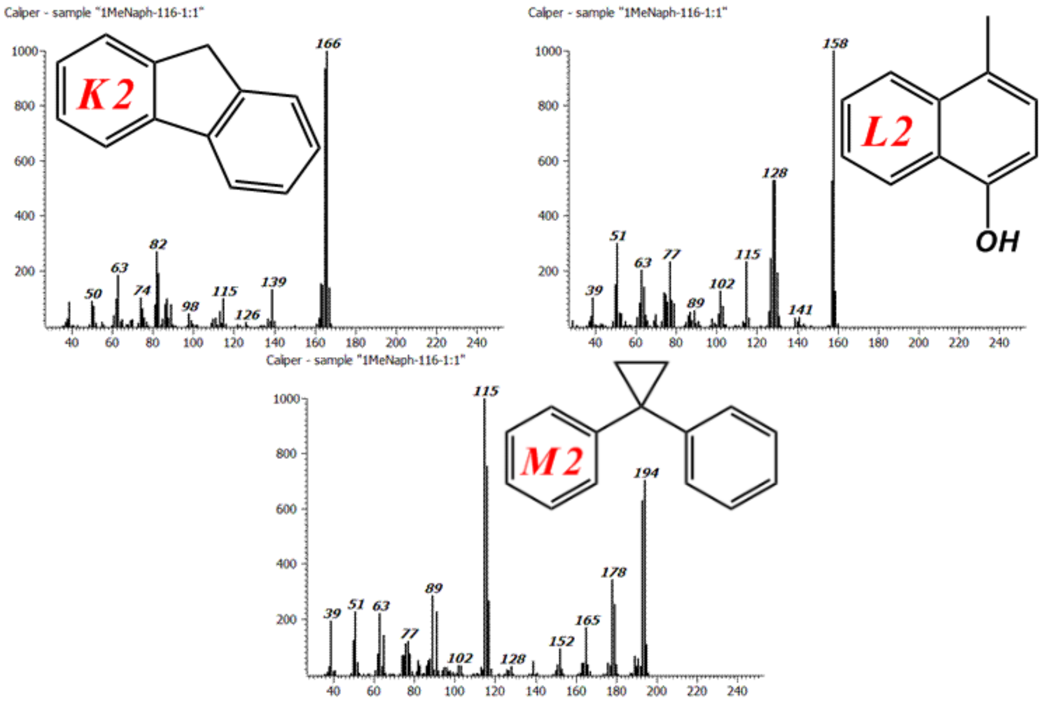


Figure C1 – Mass spectrums and chemical structure of contaminates found in 1-methylnaphthalene samples (based on GC×GC-TOFMS measurement)