CRC Report No. AVFL-29-2

EFFECT OF DHA DEVELOPMENT ON PMI VARIABILITY

Final Report

January 2022



COORDINATING RESEARCH COUNCIL, INC. 5755 NORTH POINT PARKWAY • SUITE 265 • ALPHARETTA, GA 30022

The Coordinating Research Council, Inc. (CRC) is a non-profit corporation supported by the petroleum and automotive equipment industries. CRC operates through the committees made up of technical experts from industry and government who voluntarily participate. The four main areas of research within CRC are: air pollution (atmospheric and engineering lubricants, studies); aviation fuels. and equipment heavy-duty vehicle fuels, lubricants, and performance; equipment performance (e.g., diesel trucks); and light-duty vehicle fuels, lubricants, and equipment performance (e.g., passenger cars). CRC's function is to provide the mechanism for joint research conducted by the two industries that will help in determining the optimum combination of petroleum products and automotive equipment. CRC's work is limited to research that is mutually beneficial to the two industries involved. The final results of the research conducted by, or under the auspices of, CRC are available to the public.

LEGAL NOTICE

This report was prepared by Desert Research Institute as an account of work sponsored by the Coordinating Research Council (CRC). Neither the CRC, members of the CRC, Desert Research Institute, nor any person acting on their behalf: (1) makes any warranty, express or implied, with respect to the use of any information, apparatus, method, or process disclosed in this report, or (2) assumes any liabilities with respect to use of, inability to use, or damages resulting from the use or inability to use, any information, apparatus, method, or process disclosed in this report. In formulating and approving reports, the appropriate committee of the Coordinating Research Council, Inc. has not investigated or considered patents which may apply to the subject matter. Prospective users of the report are responsible for protecting themselves against liability for infringement of patents.

FINAL REPORT

Effect of Detailed Hydrocarbon Analysis (DHA) Development on Particulate Matter Index (PMI) Variability

CRC Project AVFL-29-2

Prepared by: S. Kent Hoekman and Andrey Khlystov

> Desert Research Institute Reno, NV 89512



January 2022

Table of Contents

1.	Exe	cutive	e Summary	1			
2.	Inti	roduc	tion	5			
2	.1	Fuel	Injection Types	5			
2	.2	Fuel	Properties	5			
2	.3	PM]	Index	6			
3.	Pro	ject B	Background	7			
3	.1	Deta	iled Hydrocarbon Analysis (DHA)	7			
3	.2	Prev	ious CRC Work	7			
3	.3	Proj	ect Objectives	9			
4.	Par	ticipa	ints, Fuels, and Methods	9			
4	.1	Labo	oratory Participants	9			
4	.2	Test	Fuels	9			
4	.3	DHA	A Analytical Methods 1	.2			
4	.4	Data	a Analysis Methods 1	5			
5.	Exp	oerim	ental Results and Discussion 1	.8			
5	.1	Intra	a-Laboratory Repeatability 1	.9			
5	.2	Inter	r-Laboratory Comparisons	22			
	5.2.	.1	Total Results	27			
	5.2.	.2	Results by PIONA Group 3	;1			
	5.2.	.3	Detailed Results of Aromatics 3	;2			
	5.2.	.4	Results of Individual Compounds 3	\$4			
6.	Res	ponse	es from Participating Laboratories4	6			
7.	Sun	nmary	y and Conclusions	8			
8.	. Recommendations						
9.). References						

List of Figures

Figure 1. PMI distribution of 1445 worldwide gasolines. Taken from Aikawa et al. (2010)
Figure 2. GC column temperature profiles for different DHA methods
Figure 3. Sample bottles containing gasoline for shipment to participating laboratories
Figure 4. Nine sample bottles containing gasoline, packed in vermiculite for shipment to a participating lab
Figure 5. Metal cans, each containing nine sample bottles of gasoline
Figure 6. Example of Chain of Custody form included with sample shipment to each lab
Figure 7. Regression of PMI Factor vs. Retention Index (RI) of named compounds in SSI database
Figure 8. Intra-Laboratory Analysis of Replicate Fuels – Wt.% of All Identified Compounds (log scale)
Figure 9. Intra-Laboratory Analysis of Replicate Fuels – PMI Contributions of All Identified Compounds (log scale)
Figure 10. Total PMI values by Lab for each fuel. Top includes Lab E; Bottom excludes Lab E. 28
Figure 11. Difference in total fuel PMI values from the mean for each lab and fuel
Figure 12. PMI values of each fuel measured by each laboratory
Figure 13. Variability in PMI determination (RSD) vs. PMI level
Figure 14. Summary of wt.% (top) and PMI contributions (bottom) by PIONA group from DHA of Fuel 3
Figure 15. Wt.% (top) and PMI contribution (bottom) of aromatic constituents by carbon number for Fuel 3
Figure 16. Wt.% (top) and PMI contribution (bottom) of aromatic constituents by Laboratory for Fuel 3
Figure 17. Relative wt.% of each named component measured in Fuel 3 by each lab
Figure 18. DHA wt.% results for Fuel 1 and Fuel 6 by Lab J, and Fuel 1 by Lab A
Figure 19. Top 50 individual contributors to total PMI of Fuels 3 and 5, determined by Lab D 39
Figure 20. Wt.% results of potential co-eluting compound pairs by each lab, relative to mean results of all labs
Figure 21. Wt.% results of n-paraffins by each lab, relative to the mean of all labs
Figure 22. Lab D wt.% results showing compounds with large deviations from all lab means 44
Figure 23. Analysis of individual components in Fuels 6a and 6b by Lab F: before (top) and after (bottom) modifying sample handling procedures to minimize evaporative loss
Figure 24. PMI of Fuels 6a and 6b from DHA measurements by Lab F: before (old) and after (new) modifying sample handling procedures to minimize evaporative loss

List of Tables

Table 1. Comparison of Total Number of Gasoline Components in DHA Methods	8
Table 2. List of Market Gasoline Samples Used in CRC Project AVFL-29-2	10
Table 3. Summary of Laboratory Questionnaire Responses	13
Table 4. Examples of Common Naming Discrepancies Corrected in Final Database	16
Table 5. Parameters for Regression Equations: Log_{10} (PMI) = a + (b x RI)	18
Table 6. Summary of DHA Results by PIONA Group Type, Wt.%	23
Table 7. Summary of DHA Results by PIONA Group Type, PMI Contributions	25
Table 8. Summary of PMI Results for All Fuels	27
Table 9. Potential Co-Elution Problems Identified in ASTM D6730	40

List of Appendices

Appendix I	Questionnaire for Laboratories Providing Detailed Hydrocarbon Analysis (DHA) of Gasoline Samples
Appendix II	Compound Naming Reconciliation
Appendix III	DHA Weight % Results by PIONA Group Type and Carbon Number
Appendix IV	DHA PMI Results by PIONA Group Type and Carbon Number
Appendix V	Graphical Summaries of DHA Results (Wt.% and PMI) by PIONA Group Type
Appendix VI	Graphical Summaries of Wt.% and PMI Contributions of Aromatics by Carbon Number
Appendix VII	Graphical Summaries of Wt.% and PMI Contributions of Aromatics by Laboratory
Appendix VIII	Comparison of Individual Lab's Wt.% Results to Mean Results from All Labs for all Named Compounds
Appendix IX	Top 50 Contributors to Total PMI Determined by Each Lab for Fuel 3 and Fuel 5
Appendix X	Individual Compounds Measured by Each Lab Showing Large Deviations from Mean Values of All Labs
Appendix XI	Responses from Participating Laboratories

List of Acronyms and Abbreviations

CAS	Chemical Abstract Service (registry numbering of chemical species)
CI	Confidence Interval
CoC	Chain of Custody
CRC	Coordinating Research Council
DRI	Desert Research Institute
DBE	Double Bond Equivalent
DHA	Detailed Hydrocarbon Analysis
FID	Flame Ionization Detector
GC	Gas Chromatography
GC-MS	Gas Chromatography – Mass Spectrometry
GDI	Gasoline Direct Injection
GM	General Motors
IQR	Inter-Quartile Range
IUPAC	International Union of Pure and Applied Chemistry
LDGV	Light-Duty Gasoline Vehicle
PFI	Port Fuel Injection
PIONA	Paraffins, Iso-paraffins, Olefins, Naphthenes, Aromatics
PM	Particulate Matter
PMI	Particulate Matter Index
QC	Quality Control
RI	Retention Index
RSD	Relative Standard Deviation
SIDI	Spark Ignition Direct Injection
SSI	Separation Systems Inc.
SwRI	Southwest Research Institute

1. Executive Summary

It is known that gasoline composition has an effect on particulate matter (PM) emissions from spark ignition engines, with both chemical and physical properties of the fuel being important. A predictive equation has been developed to calculate the PM index (PMI) of a particular gasoline, meaning the relative tendency of that fuel to produce PM emissions. The total PMI value of a given gasoline is computed as the summation of the PMI contributions of all fuel constituents, which requires knowledge of each constituent's concentration, as well as its double bond equivalent (DBE) and vapor pressure. Thus, detailed speciated analysis [also called detailed hydrocarbon analysis (DHA)] of each gasoline sample is required to compute its total PMI value.

Several analytical methods are commonly used to perform DHA determination of gasoline; particularly ASTM D6729, ASTM D6730, and an enhanced version of ASTM D6730 that was recently developed by Separation Systems Inc. (SSI) as part of CRC Project AVFL-29, and is now described in Appendix 1 of ASTM D6730. An objective of the current follow-on project, AVFL-29-2, is to investigate the variability of DHA results – and PMI values calculated from these results – from analysis of a common set of marketplace gasolines. This was not a typical round robin study, in that a common analytical procedure was not specified. Instead, each participating laboratory was free to use whatever DHA method they typically employ. To further investigate potential sources of variability in the results, a laboratory questionnaire was used to understand analytical and computational details of each laboratory's method.

A total of 10 laboratories participated in this project: five CRC member companies (Aramco, Chevron, GM, Marathon, and Phillips 66) and five commercial laboratories (Gage, Intertek, SGS, SSI, and SwRI). The identities of the participating laboratories were coded using letters from A to J. Eight gasoline samples were used, all of which were supplied by CRC and were E10 marketplace fuels. To assess intra-laboratory variability, one of the 8 fuels was used as a "blind replicate" sample. Thus, each laboratory analyzed a total of 9 samples, with 2 of the 9 being the identical gasoline.

Data from analysis of each sample were submitted to DRI in whatever electronic format was typically used by the participating laboratories. Results were expressed in units of wt.% of each component in the gasoline. Considerable effort was required to develop a uniform database in which a common compound naming convention was used. As a starting point, the Master List of compounds defined by SSI in the CRC AVFL-29 project was used. This list contains 625 explicitly-named compounds and 197 generically-named compounds. Also taken from the Master List were carbon number and PMI factor for each component, as reported by SSI. Hydrocarbon group types were classified as n-paraffins, iso-paraffins, olefins, naphthenes, and aromatics (PIONA), as well as oxygenates and unidentified.

Results from each laboratory included explicitly-named, generically-named, and unidentified compounds. The method of assigning PMI factors varied among these three categories. For explicitly-named compounds, PMI factors from the SSI Master List were applied. For the other two compound categories, PMI factors were calculated from regression data of PMI vs. retention index (RI) for the 822 compounds in the SSI Master List. PMI values for generically-named compounds

were determined from regression data of the appropriate PIONA group; PMI values for unidentified compounds were determined from regression of all 822 compounds.

Analysis of the replicate fuels showed overall good intra-laboratory agreement in the wt.% results for nearly all identified compounds by all laboratories, although with a few outlier compounds. No additional analyses were conducted to investigate reasons for these outliers or to quantify the variability within or across laboratories. The total number of identified compounds in these replicate analyses was 200-300 for most labs, but only 108 compounds for Lab E, which did not identify any component eluting later than n-tridecane (C_{13}).

Total PMI values for each fuel were calculated from the wt.% results provided by the laboratories. By using the common set of compound names and PMI factors in our database, variability in total fuel PMI values can be attributed to differences in the laboratories' DHA results. Although there were a few exceptions, all labs determined a similar relative ranking of the eight fuels in terms of PMI values, with Fuels 1 and 5 being among the lowest (PMI of 1.1 - 1.2) and Fuels 3 and 4 being among the highest (PMI of 2.1 - 2.3).

For a given fuel, there was considerable variability in the PMI values as determined by the 10 labs. Lab E, which measured the fewest number of compounds – and especially the fewest heavy compounds (C_{10+}) – gave significantly lower PMI values for most fuels. This is illustrated in Figure ES-1, which shows the PMI values for each fuel determined by each lab. After excluding Lab E, the relative standard deviation (RSD) for PMI values of the remaining laboratories was in the range of 9-14% for 7 of the 8 fuels, but was over 20% for one fuel (Fuel 6). A weak relationship between RSD and PMI was seen, though this is likely not meaningful, given the large variability that was evident.



Figure ES-1. PMI of each fuel as calculated from DHA results reported by each laboratory (Letter symbols indicate Lab identities. Horizontal lines indicate mean values and 95% confidence intervals.)

Of all the PIONA compound group types, aromatics were the dominant contributors to total PMI of all the fuels. For 7 of the 8 fuels, average measured aromatics content was in the range of 22-33 wt.%, which contributed 76-83% of the total PMI. The 8th fuel (Fuel 7) had lower aromatics content (17%), but the aromatics still contributed 69% of the total PMI. In many fuels, the 2nd largest contributor to total PMI was unidentified compounds, especially for Labs C, G, H, I, and J. Because many (perhaps most) unidentified compounds are aromatic species, the total PMI contribution attributed to aromatics is probably underestimated by these labs, although their estimates of total fuel PMI are likely not greatly affected. On the other hand, failure to include unidentified components from the DHA results could significantly underestimate a fuel's PMI value, as these species are responsible for up to 10-20% of the total PMI in some cases.

Examining the aromatics results in more detail revealed that with most fuels, their mass contribution was greatest in the range of C_7 - C_9 , while their PMI contribution was greatest in the range of C_{10} - C_{12} . Inter-laboratory variability of wt.% values remained nearly constant over the entire range of aromatics, but on a PMI basis, the variability was much higher in the C_{10} - C_{12} range than in the C_7 - C_9 range. Increasing variability with carbon number results from the dramatic increase in PMI factors (due to lower vapor pressure) with molecular weight. (Assessing the validity of the compound vapor pressure data was beyond the scope of this project, though this might be useful in the future, considering the dominant influence that vapor pressure has on PMI factors of individual compounds.) Thus, it appears that a major factor driving high inter-laboratory variability in determining a fuel's total PMI value stems from differences in the laboratories' ability to measure C_{10} - C_{12} aromatics. To reduce this variability, efforts to improve measurement of these aromatics should be undertaken.

Further analyses were conducted to examine results for individual species measured by each laboratory, and to assess inter-laboratory variability in some instances. This revealed three major data problems that could contribute to overall high variability, if not corrected. First, one laboratory, while using ASTM Method D6730, measured far fewer compounds than the other labs. Many of the "missing" compounds were in the heavy ends of the fuel, which contribute disproportionately to a fuel's total PMI. Second, one lab clearly mixed-up fuel samples, reporting results for Fuel 1, when the actual fuel being analyzed was Fuel 6. Third, at least one laboratory appeared to have a volatility bias in analysis of some (but not all) fuels. It is likely that evaporative loss of light ends occurred, resulting in under-reporting of the most volatile constituents (which have low PMI factors) and over-reporting of the least volatile constituents (which have high PMI factors).

Analysis of individual compounds enabled identification of the major species contributing to the total PMI of two fuels. The top 50 species were dominated by aromatic components, particularly in Fuel 3 (which had a relatively high PMI value of 2.3) as compared to Fuel 5 (which had a relatively low PMI value of 1.2). Individual compound analysis was also used to investigate co-elution problems of specific pairs of compounds as identified in ASTM Method D6730. With few exceptions, significant co-elution problems were not apparent in this study.

The laboratory questionnaire that was distributed to all participants provided considerable information regarding analytical details of the DHA methods used. While revealing certain features that could impact inter-laboratory variability – such as column length, use of cryogenic conditions, the number of compounds measured, and the end point of the chromatographic runs – the knowledge

gained from these questionnaires does not provide a satisfying explanation of the major causes of inter-laboratory variability of PMI results.

Furthermore, based solely on the questionnaires and the analytical results from this study, it is not possible to unequivocally define one ASTM method as being superior to the others with respect to PMI determination. At the same time, it seems self-evident that a method which explicitly identifies a larger number of compounds would be preferred over one that identifies a smaller number of compounds. Thus, all other things being equal, use of the extended ASTM D6730 method would be preferred over the standard method.

The overall inter-laboratory fuel PMI variability in this study, expressed as RSD, ranged from about 10% to 20% over the eight fuels analyzed. It is likely that this variability could be reduced somewhat by using a test design in which all laboratories employed the same method. If such a study is to be conducted in the future, it is recommended that analysis of an external standard be included, whereby participants measure absolute concentrations (μ g/mL) of a set of known compounds in a standard mixture. It may also be useful to measure absolute concentrations of individual species in gasoline samples, and not limit results to a relative concentration basis of wt.%.

Finally, it's worthwhile to note that an ASTM workgroup has recently been launched with the goal of developing a DHA method to be used specifically for PMI analyses. This workgroup will oversee an inter-laboratory study to determine the C_6 - C_{14} measurement precision of the new method.

2. Introduction

Historically, particulate matter (PM) emissions from light-duty gasoline vehicles (LDGVs) have not been a major concern. In large part, this is because the induction of relatively homogeneous air/fuel combustion mixtures in gasoline engines minimizes the problems of fuel rich zones and the presence of liquid fuel in the combustion chamber, which are believed to be largely responsible for the formation of PM through diffusion burning.¹

Two recent developments have occurred that now raise concerns about gasoline vehicle PM emissions. First, modern fuel injection systems have been developed and are now commonly employed to provide improved vehicle performance and efficiency. Gasoline direct injection (GDI) systems, which inject liquid fuel directly into the combustion chamber, can lead to wall wetting or other manifestations of liquid fuel within the combustion chamber, thereby contributing to increased PM emissions. Second, because of large reductions in PM emission certification levels for all vehicle types, even very low PM emission rates are now of concern. For example, federal test procedure (FTP) PM certification levels for Tier 0 vehicles (1981-1993) were 0.20 g/mi; Tier 2 vehicles, which comprise the bulk of the current LDV fleet, have a certification level of 0.01 g/mi; Tier 3 vehicles, which entered the market in 2017, have a certification level of 0.003 g/mi.

2.1 Fuel Injection Types

While there are many variations, fuel injection technologies are commonly categorized into two types: port fuel injection (PFI) and gasoline direct injection (GDI). With PFI, liquid fuel is injected into the intake port area of the engine, from where it vaporizes and is carried into the combustion chamber along with intake air. Through years of design optimization involving nozzle geometry, charge motion, injection pressure, and other engineering features, PFI systems have become very effective in minimizing the presence of liquid fuel in the combustion chamber, thereby avoiding diffusion burning, which would produce PM emissions.

With GDI engines [also called spark ignition direct injection (SIDI)], liquid fuel is injected directly into the combustion chamber. This can create potential problems of incomplete droplet evaporation and wetting of the piston and combustion chamber walls with liquid fuel, which can lead to diffusion burning. While engineering improvements are constantly being developed to address these problems, and GDI vehicles are now able to meet the Tier 3 standard of 3 mg/mi, future PM regulations (such as the upcoming CARB regulation of 1 mg/mi) remain a significant challenge for GDI vehicles.

2.2 Fuel Properties

It has been known for some time that gasoline composition has an effect on PM emissions from spark ignition engines.^{2,3} Both chemical and physical properties are important with respect to PM formation. Different chemical constituents within gasoline have different propensities to form soot. In particular, aromatic species are more prone to form soot than are paraffinic species.^{4,5,6} Aromatics are often thought of as the nucleus around which soot growth occurs. In addition, the volatility of gasoline, represented by boiling point or vapor pressure, is critical in affecting fuel evaporation processes. The least volatile fuel species are the last to vaporize, and hence are concentrated in the residual liquid droplets or films that undergo diffusion burning in the combustion chamber. The

combination of low volatility and high aromatics (such as C_{10+} aromatic compounds) represents the worst situation with respect to PM formation.

2.3 PM Index

Some time ago, researchers from Honda published a method for predicting the tendency of a gasoline to produce PM emissions based upon its physical and chemical properties.^{7,8} This predictive equation (Eq.1) for the so-called PM Index (PMI) incorporates factors that relate to the critical fuel parameters of vapor pressure and aromatics content. In 2013, Leach et al. published a very similar formula for Particulate Number Index.⁹ In 2016, Chapman et al. described the use of several other fuel properties that correlate with PMI.¹⁰ Others have recently reviewed and summarized a variety of indices developed to relate PM emissions from gasoline engines to fuel composition.²

$$PM Index = \sum_{i=1}^{n} \frac{DBE_i + 1}{VP_i} \times Wt\%_i$$
 (Eq. 1)

In Eq. 1, the term "DBE_{*i*}" refers to the "double bond equivalent" value of gasoline specie "*i*". DBE can be considered a proxy for aromatics content. Straight chain paraffins have a DBE value of 0; cyclic paraffins and straight chain single olefinic compounds have DBE values of 1; benzene has a DBE value of 4; other aromatics could have even higher DBE values, depending upon their chemical structure. The term "VP_{*i*}" is the vapor pressure (in kPa) of specie *i* at a temperature of 443°K (170°C). Application of the PM Index predictive equation (and the similar PN Index) requires detailed compositional analysis of gasoline, since DBE and VP values are needed for each of the hundreds of species present in the fuel. The PMI value for the entire gasoline is then calculated as the sum of the mass-weighted contributions of all species.

Honda performed detailed hydrocarbon analysis (DHA) of 1445 marketplace summer grade

gasolines collected worldwide in 2008-2009 and calculated the PMI value for each one.³ (Note, the method used to determine these PMI values was ASTM D6729.) The PMI distributions of these gasolines are shown in Figure 1. While the mean PMI value was around 1.5, the high end tail of the distribution included fuels with PMI values greater than 3.0. Included in this sample set are 406 gasolines from the U.S., which showed a similar, but slightly higher skewed distribution of PMI values compared to the worldwide distribution.



3. Project Background

3.1 Detailed Hydrocarbon Analysis (DHA)

Detailed speciation of gasoline constituents [also referred to as Detailed Hydrocarbon Analysis (DHA)] has been of interest for several decades. Typically, this is conducted using high resolution gas chromatographic (GC) methods. Three existing ASTM methods used for this purpose are D6729, D6730, and D6733.^{11,12,13} In all three methods, capillary GC columns are used to separate volatile fuel constituents, which are then detected and quantified using a flame ionization detector (FID). Of these three, ASTM D6729 and ASTM D6730 (and variations of them) are the most widely used. They both utilize a 100-m capillary column of 0.25 mm inside diameter, coated with a 0.5 µm film of bonded dimethyl-polysiloxane. (This column type is also referred to as a "100% methyl" column.) The principal difference between the two methods is that ASTM D6730 includes a short pre-column of 5% phenyl/95% methyl polysiloxane (referred to as a "5% phenyl" column) which is used to modify slightly the chromatographic retention behavior of different gasoline species, thereby allowing for resolution of a few important pairs of species which otherwise co-elute and cannot be independently measured. The four most important pairs of co-elutions resolved by use of the pre-column in ASTM D6730 are the following:

- 1. 2,3-dimethylbutane and MTBE
- 2. 1-methylcyclopentene and benzene
- 3. 2,3,3-trimethylpentane and toluene
- 4. p-xylene and 2,3-dimethylheptane

For most purposes, the degree of species resolution and detection provided by ASTM D6729 and D6730 are sufficient. However, these methods may not be adequate in certain situations, such as when determining PMI values of gasoline. A particular concern with use of these ASTM methods is their inability to identify and quantify low concentrations of the heaviest (least volatile) constituents in gasoline. These heavy constituents are rich in aromatics, and therefore have relatively high PMI values. Thus, the inability to measure these species, even though they may represent only a small fraction of the total fuel mass, could result in significant underestimation of a gasoline's PMI value.

3.2 Previous CRC Work

In recognition of these problems with established DHA methods, and the impacts they could have on PMI determination, CRC recently funded a project to develop an enhanced DHA analytical method. In this CRC project, called AVFL-29, the contractor [Separation Systems, Inc. (SSI)] modified the standard ASTM D6730 method by including an additional temperature ramp for the GC column. Thus, instead of a final column temperature of 200 °C as specified in D6730, SSI's enhanced method includes an additional, rapid temperature ramp to 300 °C. This has the effect of eluting the highest boiling gasoline compounds as relatively sharp chromatographic peaks that can be integrated and quantified. Figure 2 illustrates the GC column temperature and time conditions for ASTM D6729 and ASTM D6730, as well as for SSI's enhanced DHA method. (In this report, we refer to SSI's enhanced method as D6730-Ext. ASTM Method D6730 now includes this revised method under Appendix 1.)

Also as part of CRC Project AVFL-29, SSI significantly improved the identification of chromatographic peaks, both by means of GC-MS analysis and by use of additional, authentic alkyl-substituted naphthalene compounds. In this way, SSI developed an expanded (and more reliable) list of gasoline constituents, with many more species now being uniquely defined, rather than simply defined by chemical class using a generic name, such as "C8 olefin." The complete list of 822 species in SSI's fuel database is included in their final report.¹⁴ Table 1 provides a comparison of the total numbers of gasoline species in both ASTM methods and in SSI's enhanced DHA method.



Gasoline Constituents	ASTM D6729 (Table A1.1 in method)	ASTM D7630 ^(a) (Table A1.1 in main method)	SSI Enhanced DHA (ASTM D6730-Ext.) ^(b) (Appendix D in Final Report to CRC)
Specific Names	310	308	625
Generic Names	149	123	197
No Names	-	171	-
Total	459	602	822

Table 1. Comparison of Total Number of Gasoline Components in DHA Methods

(a) These values are taken from ASTM D6730-01, which was reapproved in 2016. The recently updated version, ASTM D6730-21, contains the same total number of constituents in the main method (Table A1.1), but also includes an Appendix table containing the list of compounds provided by SSI to CRC in Project AVFL-29.

(b) These values are taken from SSI's Final Report to CRC for Project AVFL-29, dated June 2018. A few additional constituents (<10) have been added to the SSI database since that time.</p>

It is important to note that a large fraction of the additional gasoline constituents identified by SSI using their enhanced DHA method are relatively high boiling aromatics, and thus have an exaggerated impact on PMI values. As a point of comparison, compound identification using the normal ASTM D6730 method ends at the C₁₃ normal paraffin, n-tridecane. In contrast, SSI's enhanced DHA method identifies 75 compounds that elute after n-tridecane. The average DBE value of these additional 75 compounds is 5.1, indicating that they are highly aromatic. Because of this, it is expected that a gasoline analyzed by the enhanced DHA method would give a higher PMI value than the same gasoline analyzed by the standard ASTM D6730 method (or other similar methods), particularly if the gasoline contained a substantial level of "heavy ends." In the CRC AVFL-29 project, it was shown that application of SSI's enhanced DHA method increased the calculated PMI values of the five gasoline samples that were analyzed by 4% to 29%.¹⁴

3.3 Project objectives

The principal objectives of this project were to investigate the variability of DHA and PMI results obtained by GC analysis of a common set of gasolines as performed by various test laboratories, and to explore potential sources of this variability. Several types of data analysis were performed to identify which fuel components (and chemical classes of components) contribute the most to DHA and PMI variabilities. In addition, a questionnaire was provided to each test laboratory to ascertain details of the specific DHA methods being employed. Information gathered from these questionnaires was combined with the laboratories' DHA results in an effort to determine whether methodological differences could explain some of the observed lab-to-lab variability.

It is important to note that this project did not involve a classic round robin test program, in which all participants utilized the same analytical method in conducting their gasoline analyses. Furthermore, the participants were not informed that the requested DHA analyses were part of an inter-laboratory comparison program. To avoid alerting the labs to this, the questionnaire about analytical methods was not provided to a participant until after they had submitted their DHA results. The objective was to assess variability in DHA results from laboratories using whatever method they normally employ, without any effort to harmonize or limit the types of analyses being conducted.

4. Participants, Fuels, and Methods

4.1 Laboratory Participants

A total of ten laboratories participated in this project. Five laboratories were CRC member companies and five were outside commercial labs:

- CRC member companies: Aramco, Chevron, GM, Marathon, and Phillips 66.
- Commercial laboratories: Gage, Intertek, SGS, SSI, and SwRI

The identities of these participants were coded, using single letter names: A through J. Upon inquiry, each participant was informed of its own identifying code, but not the codes of any other participants.

4.2 Test Fuels

All test fuels were marketplace E10 gasolines, provided by CRC member companies with the sources noted in Table 2. Gasolines were selected to cover a range of PMI values. At the start of the project, 6 gasolines were provided, but 2 more were added later. Two of these test fuels were used in a previous CRC project (AVFL-27-2), four were part of a market survey by the Alliance of Automobile Manufacturers (Auto Alliance), and two were provided by Aramco. (Note: the Auto Alliance has been reorganized and renamed: Alliance for Automotive Innovation.) All 8 test gasolines are identified in Table 2, which also indicates a relative PMI value. These PMI ratings of low (<1.5), medium (1.5-2.0), and high (>2.0) were assigned based on estimates provided by the fuel supplier. Calculation of more precise PMI values for each fuel was done as part of this project, based on the detailed chemical speciation data provided by the participating labs.

To assess intra-laboratory variability, one of the 8 gasolines was selected as a "blind repeat" sample. Thus, each laboratory received 9 gasoline samples for DHA analysis, with 2 of the 9 being identical. Gasoline No. 6 was chosen as the blind repeat sample. However, due to insufficient supply, one of the laboratories (Lab E) received Gasoline No. 4 as the blind repeat.

No.	Grade	Location	Source	Estimated PMI *	
1	Premium winter	California	CRC AVFL-27-2	Low	
2	Regular summer	Regular summer Atlanta Auto Alliance		Medium	
3	Regular summer	Detroit	Auto Alliance	High	
4	Regular summer	San Antonio	Auto Alliance	High	
5	Regular summer	Georgia	CRC AVFL-27-2	Low	
6	Regular	-	Aramco	High	
7	Regular summer	Houston	Auto Alliance	Medium	
8	Regular	-	Aramco	High	

 Table 2. List of Market Gasoline Samples Used in CRC Project AVFL-29-2

* Low = <1.5; Medium = 1.5-2.0; High = >2.0

In preparation for shipping, aliquots were removed from each gasoline container and placed into smaller bottles with tightly sealing plastic caps. Different sized bottles were used for different labs, as each lab had its own sample volume requirements. A photo of four sample bottles is shown in Figure 3. The parafilm wrapped around each bottle cap provided an additional layer of protection, although the main seal preventing sample leakage was provided by the Teflon-lined cap itself. Subsequently, it was learned that a few of the sample bottles leaked during shipment to the participating labs. This probably resulted from pressure changes that occurred during air transport. In cases of leakage, replacement samples were prepared and shipped. As an extra precaution, the bottle caps were screwed more tightly, and were secured with a wrapping of adhesive tape.



Figure 3. Sample bottles containing gasoline for shipment to participating laboratories. (Note sample bar code label visible on 3rd bottle from the left.)

The sample bottles prepared in DRI's laboratory were individually wrapped in plastic zip-lock bags, then packed inside 1-gallon metal paint cans, using vermiculite as packing material. Figure 4 shows a photo of such a can containing 9 gasoline samples to be shipped to a participating lab. Figure 5 shows a photo of several filled cans, stored in a refrigerator, awaiting shipment. These sample cans were shipped overnight in a refrigerated package (with re-usable ice packs) to each participating laboratory.



Figure 4. Nine sample bottles containing gasoline, packed in vermiculite for shipment to a participating lab.



Figure 5. Metal cans, each containing nine sample bottles of gasoline. Cans were stored in a refrigerator, awaiting shipment to participating labs.

To track all test gasoline samples, DRI employed an established numbering scheme and chain of custody (CoC) protocol. An example of the chain of custody form that was included with each

sample shipment is shown in Figure 6. The nine tracking numbers for the nine fuel samples are shown on this form. For historical reasons, DRI refers to these tracking numbers as "PMI numbers," as they are coded to indicate <u>P</u>roject, <u>M</u>edia, and <u>I</u>nstrument. These PMI identification numbers should not be confused with the PMI values of the gasolines.

Chain of custody form									
Andrey Khlystov (andrey.khlystov@dri.edu) Desert Research Institute 2215 Raggio Parkway Reno, NV 89512									
Comple #	DM	Initials	Sample Volume	Shin Data	Requested	data Resigned	Pessived by	commonte	
Sample #	PIVII	CP	(mi)	7/17/2020		date Recieved	Received by	comments	
Fuel 2	P179M001091	CB	30	7/17/2020	ASTM D6730				
Fuel 3	P179M001I093	CB	30	7/17/2020	ASTM D6730				
Fuel 4	P179M001l094	CB	30	7/17/2020	ASTM D6730				
Fuel 5	P179M001I095	CB	30	7/17/2020	ASTM D6730				
Fuel 6	P179M001I096	СВ	30	7/17/2020	ASTM D6730				
Fuel 7	P179M001I097	CB	30	7/17/2020	ASTM D6730				
Fuel 8	P179M001I098	CB	30	7/17/2020	ASTM D6730				
Fuel 9	P179M001I099	CB	30	7/17/2020	ASTM D6730				
		Ship to		Russ Lewis Marathon R 11631 US Ro Catlettsburg 606-921-200	efining Logistics S bute 23 ;, KY 41129 09	Services			

Figure 6. Example of Chain of Custody form included with sample shipment to each lab.

4.3 DHA Analytical Methods

Each laboratory conducted DHA analyses of the gasoline samples using its standard procedures. Consequently, a variety of different methods were used by the entire group of participants. To gain an understanding of these methods, each participant was asked to complete a laboratory questionnaire (after their DHA results had been submitted) designed to provide key methodological information. The questionnaire, which was developed with input by the CRC, is shown in Appendix I. Not all laboratories fully completed the questionnaire, as some information was considered proprietary.

A summary of information obtained from the lab questionnaires is provided in Table 3. While this table does not include responses to all items on the questionnaire, it contains what we believe to be the most important factors describing the DHA methods used by each participant. The methodological differences documented in Table 3 may contribute (and help explain) lab-to-lab variability in the DHA analytical methods.

Lab Code	Approx. ASTM Method (1)	Column Length	Pre- Column	Cryogenic start temp.	Detector Type	Carrier Gas Type	Carrier Gas Control	GC Instrument	Software	Handling of unidentified peaks	Use of RRF for quantifi- cation	Adjustment for Ethanol	No. of PIONA compounds identified (2)	Approx. No. of Identified Cmpds (3)	Typical wt. % of unidentified compounds	RI of last identified peak (4)
A	D6730	100m	No	No	FID + MS	He	Constant Flow rate	Agilent 6890	Hydrocarbon Expert Ver. 4.2	reported as unidentified	Yes	None	15/130/50/130/130	456	<3%	1661
В	D6730-Ext	100m	Yes	Yes	FID only	H2	Constant Flow rate	ThermoFisher Trace 13410	Chromquest and Dragon DHA	reported as unidentified	Yes	None	20/283/180/88/300	872	<0.5%	1958
с	D6730	100m	Yes	Yes	FID only	He	Constant Pressure	Agilent 7890N	Dragon DHA	reported as unidentified	Yes	None	13/68/112/48/62	304	2%	1552
D	D6730-Ext	100m	Yes	Yes	FID + MS	He	Constant Pressure	Agilent 6890	Hydrocarbon Expert Ver. 5.29	reported as unidentified	Yes	Ethanol by ASTM D4815	18/147/244/131/258	799	<1.0%	1718
E	D6730	100m	Yes	Yes	FID only	He	?	Agilent 7890B	Separation System	unidentified peaks not included	No	?	15/100/30/80/80	306	0.01-30%	1300
F	D6730-Ext	100m	Yes	Yes	FID + MS	He	Constant Pressure	Agilent 7890B	Hydrocarbon Expert	reported as unidentified	Yes	None	16/188/247/132/226	810	<0.5%	1796
G	D6729	40 m	No	No	FID only	H2	Constant Pressure	Agilent 7890B	Hydrocarbon Expert	reported as unidentified	Yes	Ethanol by ASTM D4815	15/120/150/90/160	536	1-3%	2030
н	D6730	100m	Yes	Yes	FID only	He	Constant Pressure	Agilent 7890	Dragon DHA	reported as unidentified	Yes	None	15/117/162/52/85	432	<2%	1524
I	D6729	100m	No	No	FID only	Не	Constant Pressure	Agilent 6890	AC DHA	reported as unidentified	Yes	Peak splitting and tangent skimming	15/102/90/70/62	340	2-8%	1603
J	?	100m	Yes	No	FID only	Не	Constant Pressure	Agilent 6890N	Dragon DHA	reported as unidentified	Yes	None	15/100/153/79/65	413	<2%	1575

(1) ASTM D6729 = rapid ramp to 250°C; ASTM D6730 = slower ramp to 200°C; ASTM D6730-Ext = final ramp to 300°C

(2) PIONA = n-Paraffins, i-Paraffins, Olefins, Naphthenes, Aromatics. These values indicate the number of compounds identified by each laboratory's method

(3) Approximate number of identified compounds defined as identified PIONA compounds plus ethanol

(4) Retention index of last identified peak taken from DHA results for fuels in this study

Examination of Table 3 shows numerous differences in the analytical methods used by the 10 laboratory participants. The 2nd column indicates an "Approximate ASTM Method." This designation was made based on explicit naming by the participant or by our interpretation of the specific GC column temperature conditions. As shown in Figure 2, ASTM D6729 involves a relatively rapid temperature ramp to 250 °C; ASTM D6730 involves a slower temperature ramp to 200 °C; ASTM D6730 ext has an identical temperature ramp to ASTM D6730, but includes a final rapid ramp to 300 °C. Two of the 10 participants used ASTM D6729, 4 used ASTM D6730, three used ASTM D6730-Ext, and one did not indicate the method they used, citing proprietary information.

Nine of the 10 labs used a 100-m capillary GC column, while Lab G used a 40-m column. Seven of the 10 labs used a short pre-column, while 3 did not. Six labs used initial column cooling to begin the chromatographic analysis at sub-ambient temperature, while 4 labs did not. Only 3 labs (A, D, and F) indicated that both FID and MS detectors were used for peak identification, while 7 labs used only FID. Table 3 also shows considerable variability with respect to GC carrier gas type (H₂ or He), control of carrier gas flow (constant flow rate or constant pressure), GC instrument type, data analysis software, and other parameters.

The stated number of identifiable compounds varied considerably across the 10 participating laboratories – from a low near 300 for Labs C and E, to a high of near 800 for Labs B, D, and F. These three high labs (B, D, and F) used the extended ASTM D6730 method, with the more expansive list of compounds appearing in Appendix 1 of the method. In the analytical results provided in this study, most labs reported a much smaller number of identified compounds in each fuel than listed in Table 3. Typically, these identified compounds are classified as n-Paraffins, Isoparaffins, Olefins, Naphthenes, and Aromatics (PIONA). The number of PIONA components claimed to be identified by each laboratory's method is also shown in Table 3. The number of total identified compounds shown in this table is the sum of identified PIONA compounds plus ethanol.

While GC retention time is determined for each chromatographic peak, use of retention index (RI) is commonly used for peak identification purposes. As GC columns age and other chromatographic parameters vary, retention times of eluting peaks tend to "wander," making peak identification more difficult. In contrast, RI values remain more constant, which increases the reliability of peak identification. In this project, Kovats RI values were used – either as reported directly from the laboratories or as calculated by DRI, based on the retention times reported. The formula for calculating Kovats RI values is shown below:

 $RI_i = 100 \ x \ (n + (log(t_i) - log(t_0))/(log(t_{n+1}) - log(t_0)))$

Where: RI_i = retention index of component i

- n = carbon number of n-paraffin
- t_i = retention time of component i
- t_n = retention time of preceding n-paraffin
- t_{n+1} = retention time of next n-paraffin

The final column in Table 3 shows the RI value of the last eluting identified compound in each lab's analysis of the fuels used in this project. This gives some indication of the lab's ability to measure "heavy ends" of gasoline. Lab E had a much shorter final RI value of 1300, compared to the other

labs, which were all greater than 1500. Consequently, Lab E did not quantify any gasoline constituents that eluted later than n-tridecane (C_{13} n-paraffin), whereas all other labs measured compounds eluting later than n-pentadecane (C_{15} n-paraffin). This indicates that Lab E was not able to quantify some of the heavy aromatic compounds, which contribute disproportionately to the total gasoline PMI value.

Another important methodological difference of Lab E was its handling of unidentified GC peaks. As shown in Table 3, Lab E indicated that it did not include unidentified peaks. However, we found that a few unidentified peaks were included in some fuel analyses, although the total number (and mass) of these peaks was substantially less than from the other labs. This is partly due to the fact that Lab E did not report any peaks eluting after n-tridecane (C_{13}), whereas most other labs reported numerous unidentified peaks after C_{13} . Because Lab E did not include many unidentified peaks in their reported results, their mass % of identified compounds was biased high. Due to these methodological differences, Lab E was excluded from some of the inter-laboratory comparative analyses that are discussed later.

4.4 Data Analysis Methods

DHA results submitted by the participants were provided in a variety of electronic formats. Additionally, each laboratory utilized its own library of identified compounds and naming convention. Thus, an essential first step was to combine all the laboratories' results into a single, uniform database, which could be used subsequently for additional data analysis.

As a starting point, this database utilized the component Master List defined by SSI in their June 2018 final report to CRC for Project AVFL-29. This list (which now also appears in Appendix 1 of ASTM D6730) contained 625 specifically-named and 197 generically-named compounds, arranged in retention time order. Besides retention time (and retention index), parameters provided for each component included carbon number, hydrocarbon group type, molecular weight, vapor pressure, number of double bond equivalent (DBE), and PMI factor. Since the 2018 report was issued, SSI has added a few more compounds (<10) to their Master List. These additional compounds are also included in our database.

Compound group type was defined for each species as being in 1 of 7 compound families. Besides the 5 usual classifications of n-paraffins, iso-paraffins, olefins, naphthenes, and aromatics (PIONA), group types were included for oxygenates (designated "X") and unknowns (designated "U").

A major effort was involved in naming (or re-naming) compounds reported by each participating laboratory to fit within the database structure that was based on SSI's naming convention. In some cases, simple differences in terminology were used for the same compound. For instance, "isoprene" was used instead of "2-methyl-1,3-butadiene," or "1,3-dimethylbenzene" was used instead of "m-xylene." A list of 20 of these simple naming discrepancies is shown below in Table 4. Many other naming discrepancies were more subtle, such as including a hyphen ("dimethyl") or not including a hyphen ("dimethyl"). Considerable effort was required to identify and correct such minor changes. Appendix II documents all 144 naming changes we applied to individual laboratory's compound lists to create the final, comprehensive database. Note that corrections were made only to reconcile the naming of compounds reported to be present in the gasoline samples that were analyzed – not to reconcile all names appearing in each laboratory's complete library of compounds.

Compounds reported by each laboratory were noted as being in one of three classes: (1) explicitlynamed compounds, (2) generically-named compounds, and (3) unidentified. Explicitly-named compounds have unambiguous, complete chemical names, consistent with the naming convention used by SSI. [Note: Explicit names are not necessarily IUPAC names, and are not linked to CAS numbers.] Generically-named compounds are identified by PIONA group type and carbon number, but without a specific chemical name. Unidentified compounds do not have a PIONA group type, though they may have a carbon number. For laboratory intercomparison purposes, some analyses used only explicitly-named compounds, while other analyses used both explicitly- and genericallynamed compounds. To investigate the impacts of unidentified species, some analyses were performed with and without this class of compounds.

Participating Lab Name	Database Name
Cyclopentadiene	1,3-cylcopentadiene
1,2-ethyl-i-propylbenzene	1-Ethyl-2-i-propylbenzene
1,4-ethyl-i-propylbenzene	1-Ethyl-4-i-propylbenzend
1,2-methylethylbenzene	1-methyl-2-ethylbenzene
1,2-methyl-i-propylbenzene	1-Methyl-2-i-propylbenzene
1,2-methyl-n-butylbenzene	1-Methyl-2-n-butylbenzene
1,3-methylethylbenzene	1-Methyl-3-ethylbenzene
1,4-methyl-i-propylbenzene	1-Methyl-4-i-propylbenzene
1,4-ethyl-t-butylbenzene	1-Methyl-4-t-butylbenzene
isoprene	2-Methyl-1,3-Butadiene
4-methyl-c-pentene-2	2-Pentene-CIS- ,4-methyl
c-nonene-3	cis-3-Nonene
1,3-dimethylbenzene	m-Xylene
1,2-dimethylbenzene	o-Xylene
1,4-dimethylbenzene	p-Xylene
2,3-dimethylpentene-1	1-Pentene, 2,3-dimethyl-
Hexane, 2,2,5-trimethyl-	2,2,5-Trimethylhexane
Heptane, 3,5-dimethyl-	3,5-Dimethylheptane
4-methyl-3-heptene	3-Heptene, 4-methyl-
c-Nonene-3	cis-3-Nonene

Table 4. Examples of Common Naming Discrepancies Corrected in Final Database

Component PMI values were taken from the SSI Master List for all explicitly-named compounds. Unlike some previous definitions of PMI, the contributions of compounds that were not fully identified were also included in determining total PMI values. For these generic and unidentified compounds, PMI values were assigned based on regression analyses of PMI values vs. RI for all compounds included in the SSI Master List. The regressions we utilized are shown graphically in Figure 7. The top panel of Figure 7 shows a single, overall regression of all Master List compounds; the bottom panel shows separate regressions for each PIONA group. When assigning PMI values, the PIONA-based regressions were used for generically-named compounds, because their group types were known. For unknown compounds (where group types are not known) the overall, single regression was used to assign PMI values.



Figure 7. Regression of PMI Factor vs. Retention Index (RI) of named compounds in SSI database. Top – regression of all compounds together; Bottom – regression by PIONA group (P = Paraffins, I = Iso-paraffins, O = Olefins, N = Naphthenes, A = Aromatics, X = Oxygenates)

Equations for the regression lines shown in Figure 7 are given in Table 5. Each least-squares regression equation is of the same form: Log_{10} (PMI) = a + b x RI. The values for parameters "a" and "b" are shown, along with their error terms, and R² values to indicate the degree of overall fit.

PIONA	Ter	m a	Ter	D ²	
Group Type	value	error	value	error	K-
Р	-5.21364	0.204551	0.003027	0.000189	0.941
I	-4.20468	0.061555	0.002174	6.55E-05	0.897
0	-4.28584	0.053121	0.002589	6.94E-05	0.884
Ν	-4.07016	0.082195	0.002419	9.85E-05	0.828
А	-4.16139	0.082142	0.002864	6.69E-05	0.915
х	-3.44661	0.212342	0.00119	0.000383	0.580
all	-4.59812	0.042542	0.002958	4.33E-05	0.881

Table 5. Parameters for Regression Equations: Log₁₀ (PMI) = a + (b x RI)

The assignment of PMI factors to unidentified compounds in the results from Lab G require further explanation. This lab used a shorter GC column with the relatively fast temperature ramp of ASTM D6729. Consequently, the chromatographic peaks in Lab G's analyses were compressed into a shorter total time window compared to most other labs. (The use of H₂ as carrier gas may also have contributed to the relatively compressed chromatograms.) For unidentified compounds eluting prior to n-pentadecane (C₁₅), individual RI values were provided, to which we applied the regressions shown in Figure 7 to calculate PMI values. However, all unidentified peaks eluting after C₁₅ were summed together, with only a total wt.% value being reported for the sum. To assign a PMI value to these heavy unidentified species, we used the total regression line shown in the top panel of Figure 7 and an assumed RI value of 1500. This meant that all C₁₅₊ unidentified compounds in Lab G's analyses were assigned a PMI value of 0.87. This approach likely introduces a small low bias to the PMI values from Lab G, particularly for fuels having a substantial abundance of C₁₅₊ components, many of which are likely aromatics.

5. Experimental Results and Discussion

A large amount of data was generated by the 10 participating laboratories who each conducted DHA analysis of 9 gasoline samples. Numerous types of data analyses were performed to examine these data, compare and contrast results across labs, and determine possible factors contributing to variability within the results.

DHA results from each lab were reported on a wt.% basis for each individual constituent. All labs, except Lab E, included wt.% values for unidentified chromatographic peaks. Also, the labs all normalized their total compound results to 100%. In some cases, this can introduce a significant bias in a lab's results. For example, if light ends of a gasoline sample were lost due to evaporation, results for the heavy ends would be biased high. Alternatively, if a lab was unable to quantify heavy constituents (such as Lab E, which quantified nothing heavier than C₁₃), their light end results would be biased high.

The wt.% results, and corresponding PMI results, were analyzed on several levels. At the highest level, total results for each fuel were examined. These results were further disaggregated to assess wt.% and PMI values by PIONA group type, with particular focus on aromatics. Further analysis examined wt.% and PMI results with respect to gasoline component volatility, as determined by RI value or carbon number. Finally, analyses of individual species were conducted. Results of all these data analysis efforts are documented in tabular and graphical forms, in the sections below.

5.1 Intra-Laboratory Repeatability

Although unknown to the laboratory participants, each lab received duplicate aliquots of one gasoline sample. Fuel 4 was duplicated for Lab E; Fuel 6 was duplicated for all other labs. Analysis of results from these duplicate samples were examined to assess the intra-laboratory repeatability within each laboratory.

Figure 8 provides a direct comparison of the wt.% values reported by each lab for every identified compound (both explicitly-named and generically-named) in the duplicate samples. Note that a logarithmic scale is used in Figure 8. For most compounds, the replicate analyses were in very good agreement, as shown by the data points clustering around the 1/1 correspondence line. As expected, agreement between replicate analyses is better for compounds present in high concentration compared to those at low concentration.

Lab E stands out in Figure 8, in that it shows relatively few data points for compounds present at concentrations less than 0.1 wt.%. (The cluster of compounds near 0.001% reported by Lab E remains unexplained.) Part of the reason for this is that Lab E quantified no chromatographic peaks with RI values exceeding 1300 (eluting later than n-tridecane). Most other labs reported a significant number of low concentration compounds with RI greater than 1300. These later eluting peaks are predominantly aromatic compounds, which have relatively high PMI values.

Despite the overall good replicate agreements seen in Figure 8, several labs showed outlier points that they may wish to investigate further. For example, the red circled points shown for Labs B, D, E, H, and J represent compounds where the replicate concentration results differed by at least an order of magnitude. These outlier compounds are identified below:

- Lab B: 2,6-dimethylheptene-1
- Lab D: t-nonene-3
- Lab E: 2-methyloctane
- Lab H: 2-methylbutene-2
- Lab J: t-2,2,5,5 tetramethylhexene-3

Figure 9 provides a direct comparison of the PMI contribution of each identified compound in the duplicate samples. PMI contribution is defined as the wt.% of the individual compound in the fuel multiplied by the PMI value for that compound. As with the wt.% comparisons, these PMI comparisons show overall good agreement between the replicate samples, although a few outlier points are clearly seen. The red circled points for Labs B, D, E, H, and J highlight the same outliers as defined above in Figure 8.While beyond the scope of this project, individual laboratories are encouraged to investigate their own outlier points, and determine whether these result from mis-identification of certain chromatographic peaks.



Figure 8. Intra-Laboratory Analysis of Replicate Fuels – Wt.% of All Identified Compounds (log scale) (Fuel 4 used as replicate by Lab E; Fuel 6 used as replicate by all other labs)



Figure 9. Intra-Laboratory Analysis of Replicate Fuels – PMI Contributions of All Identified Compounds (log scale) (Fuel 4 used as replicate by Lab E; Fuel 6 used as replicate by all other labs)

5.2 Inter-Laboratory Comparisons

To compare DHA results across the 10 participating laboratories, the detailed reports provided by each lab were first combined and summarized by PIONA group type and by carbon number. Summary tables of DHA wt.% results for each fuel are provided in Appendix III, with each fuel being shown as a separate table. (Note: Lab E did not analyze Fuel 6b, which is a replicate of Fuel 6a.) Summary tables of PMI contributions by PIONA group type and carbon number are provided in Appendix IV.

The inter-laboratory results shown in Appendix III and Appendix IV were analyzed for outliers using Tukey's rule.¹⁵ According to this rule, the distribution of results for a given fuel, group type, and carbon number is divided into quartiles. The interquartile range (IQR) is the difference between the first quartile and the third quartile (IQR = Q3-Q1). A particular data point is considered an outlier if it lies more than 1.5 x IQR above the 3rd quartile or below the 1st quartile. In both Appendix III (wt.% values) and Appendix IV (PMI values) approximately 10% of the cell entries are identified as outliers, with about one-half of these outliers being attributed to Lab E. As expected, there is a strong similarity in the patterns of outliers shown in Appendix III and Appendix IV.

These appendix tables are further summarized by lumping all carbon number results into the appropriate PIONA class. The PIONA summaries for all fuels and labs are shown in Table 6 (wt.% results) and Table 7 (PMI contributions). Outlier points (identified by the same method described above) are also indicated in Table 6 and Table 7.

Fuel No.	PIONA group	Lab A	LAB B	Lab C	Lab D	Lab E	Lab F	Lab G	Lab H	Lab I	Lab J	Mean	Std. Dev.
	р	5.97	6.87	6.95	7.12	9.05	7.22	6.68	7.27	6.86	16.61	8.06	2.95
	i	50.56	48.07	46.86	45.43	44.98	49.82	46.12	48.21	46.98	30.88	45.79	5.25
	ο	5.35	6.95	6.59	9.53	5.64	6.13	6.17	7.40	6.63	5.73	6.61	1.14
	n	7.77	6.46	5.86	6.13	7.12	5.68	6.67	5.99	6.13	9.98	6.78	1.22
1	а	22.50	21.03	20.62	19.92	22.13	20.56	22.56	19.51	20.60	28.13	21.76	2.35
	x	7.82	10.55	11.29	11.23	11.07	10.40	11.04	10.88	10.90		10.58	1.01
	u	0.03	0.07	1.83	0.65	0.00	0.21	0.77	0.74	1.90	8.66	1.49	2.48
	Total	100.00	100.00	100.00	100.00	100.00	100.01	100.00	100.00	100.00	100.00		
	р	13.00	11.65	11.38	12.17	14.44	11.93	11.69	11.84	11.71	12.35	12.22	0.86
	i	33.19	31.92	30.82	31.37	30.68	30.79	29.79	31.39	31.85	32.00	31.38	0.89
	ο	7.88	8.34	7.59	7.66	6.65	7.21	7.31	8.87	7.52	15.62	8.46	2.46
2	n	11.14	9.95	9.49	10.11	8.39	10.98	10.65	9.85	8.89	9.85	9.93	0.82
-	а	25.02	27.55	27.03	27.44	29.77	28.89	28.16	25.80	25.08	26.72	27.15	1.48
	х	9.68	10.17	10.58	10.71	9.56	10.08	10.42	10.00	10.38		10.17	0.37
	u	0.10	0.42	3.11	0.54	0.51	0.13	1.98	2.24	4.58	3.44	1.70	1.52
	Total	100.00	100.00	99.99	100.00	100.00	100.01	100.00	100.00	100.00	100.00		
	р	8.59	8.55	8.21	8.65	10.37	8.72	8.42	8.23	8.36	9.48	8.76	0.64
	i	33.12	31.83	30.41	30.16	32.04	30.17	30.11	27.84	31.39	32.62	30.97	1.47
	ο	6.87	7.54	6.72	7.03	5.62	6.57	6.47	11.65	6.32	7.55	7.23	1.57
3	n	12.51	9.24	9.38	9.82	7.57	10.28	10.54	10.38	8.51	10.45	9.87	1.26
	а	29.28	32.28	31.12	33.01	34.84	33.80	32.63	29.47	29.17	33.18	31.88	1.91
	x	9.60	10.10	10.27	10.31	9.56	10.24	10.16	9.33	9.83		9.93	0.34
	u	0.03	0.46	3.89	1.02	0.00	0.21	1.66	3.09	6.42	6.73	2.35	2.45
	Total	100.00	100.00	100.00	100.00	100.00	99.99	100.00	100.00	100.00	100.00		
	р	9.95	10.25	10.08	10.70	12.22	10.55	10.16	10.59	10.34	10.75	10.56	0.61
	i	30.40	29.13	28.62	28.60	28.52	28.24	28.23	25.84	30.44	29.92	28.79	1.27
	ο	8.74	8.39	8.24	8.37	6.96	8.25	8.13	12.54	7.91	9.45	8.70	1.41
4	n	10.32	7.46	7.34	7.79	6.54	7.80	8.07	7.75	6.76	7.52	7.73	0.97
	а	31.49	33.82	32.37	33.50	35.53	34.51	33.43	30.60	29.78	33.77	32.88	1.71
	x	8.99	10.27	10.45	10.39	8.83	10.37	10.12	9.88	10.23		9.95	0.58
	u	0.10	0.68	2.90	0.66	1.39	0.30	1.85	2.80	4.55	8.60	2.38	2.46
	Total	99.99	99.99	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00		
	р	11.00	8.67	8.53	8.91	10.65	7.54	8.56	8.94	/./1	9.30	8.98	1.06
	I	39.44	38.85	38.54	31.98	34.43	40.15	37.25	39.84	38.20	39.85	37.85	2.53
	0	7.16	5.52	4.68	4.42	3.50	3.87	4.38	5.02	4.45	6.59	4.96	1.10
5	n	4.94	5.32	4.54	12.79	4.98	4.84	5.30	4.76	4.94	4.56	5.70	2.38
	a	26.62	31.04	31.47	30.87	30.87	33.38	33.32	30.63	32.61	33.13	31.99	2.50
	X	10.79	10.23	1.00	TO'03	9.57	10.04	10.42	10.13	1.04	6 50	1.30	0.35
	u Tatal	0.05	00.00	1.05	0.33	100.00	100.00	0.//	0.68	1.84	0.58	1.25	1.88
	Total	100.00	99.99	100.01	100.00	100.00	100.00	100.00	100.00	100.00	100.00		

Table 6. Summary of DHA Results by PIONA Group Type, Wt.%

Fuel No.	PIONA group	Lab A	LAB B	Lab C	Lab D	Lab E	Lab F	Lab G	Lab H	Lab I	Lab J	Mean	Std. Dev.
	р	20.67	16.67	15.47	17.39	12.20	13.12	16.59	16.92	16.51	16.82	16.24	2.21
	i	33.72	29.95	29.40	29.76	28.29	27.61	28.89	30.67	30.55	30.92	29.98	1.60
	о	5.24	5.78	4.94	4.88	6.85	4.12	4.82	5.50	4.80	5.77	5.27	0.71
	n	10.12	9.57	9.42	9.51	6.18	10.29	10.27	10.00	8.62	9.75	9.37	1.16
6a	а	19.93	26.84	26.64	27.04	35.65	33.22	27.40	23.95	23.97	27.85	27.25	4.27
	x	10.30	10.91	11.09	11.00	9.98	11.45	10.64	10.05	10.70		10.68	0.47
	u	0.02	0.31	3.05	0.43	0.84	0.19	1.40	2.90	4.85	8.90	2.29	2.67
	Total	100.00	100.01	100.01	100.00	100.00	100.00	100.00	100.00	100.00	100.00		
	р	21.48	16.71	15.64	16.95		13.14	16.57	15.94	16.05	17.55	16.67	2.07
	i	33.00	30.28	29.36	29.70		27.46	29.06	29.98	30.41	31.55	30.09	1.47
	ο	5.10	5.54	4.99	4.97		4.14	4.66	5.88	4.76	5.61	5.07	0.51
ch	n	9.87	9.62	9.37	9.57		10.69	10.35	9.99	8.69	9.79	9.77	0.54
00	а	19.23	26.27	26.51	27.42		33.18	27.31	25.87	24.33	27.84	26.44	3.43
	х	11.28	11.14	11.01	11.04		11.27	10.66	10.52	10.77		10.96	0.27
	u	0.04	0.44	3.12	0.35		0.14	1.38	1.83	4.98	7.66	2.22	2.47
	Total	100.00	99.99	100.00	100.00	0.00	100.01	100.00	100.00	100.00	100.00		
	р	8.75	8.40	7.82	8.52	10.36	8.09	8.09	8.08	7.96	8.81	8.49	0.70
	i	42.41	43.09	41.53	43.64	41.50	44.18	41.07	42.86	42.15	43.60	42.60	0.99
	0	10.17	7.97	7.22	7.83	6.37	6.55	6.83	8.20	6.99	8.71	7.68	1.10
7	n	13.00	11.42	10.74	11.25	10.60	11.27	12.19	11.41	10.02	11.42	11.33	0.79
-	а	14.29	17.42	17.39	17.11	19.53	18.79	18.59	16.66	16.45	18.63	17.48	1.43
	х	11.06	10.93	10.63	10.62	11.65	10.87	10.35	10.26	10.29		10.74	0.42
	u	0.32	0.75	4.67	1.04	0.00	0.27	2.87	2.54	6.14	8.83	2.74	2.81
	Total	99.99	99.98	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00		
	р	14.55	14.99	13.42	15.14	18.68	13.12	14.70	14.74	13.76	15.75	14.88	1.48
	i	30.64	30.71	29.24	29.46	31.10	28.43	29.07	26.05	30.64	29.93	29.53	1.42
	0	5.76	6.94	6.21	6.25	4.69	5.66	5.98	10.56	5.96	13.27	7.13	2.53
8	n	11.84	8.34	8.74	8.91	6.36	9.55	9.71	9.29	7.90	9.06	8.97	1.33
	а	27.62	26.58	27.04	27.88	28.72	30.87	27.42	24.50	24.82	28.77	27.42	1.78
	х	9.46	11.93	11.74	11.68	10.46	12.22	11.28	10.96	11.45	_	11.24	0.80
	u	0.14	0.50	3.60	0.69	0.00	0.16	1.83	3.91	5.47	3.23	1.95	1.86
	Total	100.01	99.99	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00		

Notes: P = n-paraffins; I = i-paraffins; O = olefins; N = naphthenes; A = aromatics, X = oxygenates; U = unidentified Fuels 6a and 6b were replicate samples for all labs except Lab E Shaded cells indicate outlier values

Fuel No.	PIONA group	Lab A	LAB B	Lab C	Lab D	Lab E	Lab F	Lab G	Lab H	Lab I	Lab J	Mean	Std. Dev.
	р	0.011	0.011	0.010	0.011	0.010	0.015	0.011	0.013	0.014	0.034	0.014	0.007
	i	0.127	0.116	0.103	0.105	0.066	0.119	0.104	0.106	0.101	0.063	0.101	0.020
	ο	0.008	0.016	0.015	0.023	0.007	0.013	0.013	0.018	0.013	0.019	0.014	0.005
1	n	0.064	0.039	0.027	0.025	0.023	0.021	0.030	0.027	0.034	0.051	0.034	0.013
1	а	0.914	0.911	0.790	0.841	0.592	0.914	0.979	0.675	0.748	1.482	0.885	0.229
	x	0.009	0.012	0.013	0.013	0.013	0.012	0.013	0.013	0.013		0.012	0.001
	u	0.000	0.002	0.200	0.140	0.000	0.018	0.121	0.036	0.101	0.429	0.105	0.127
	Total	1.134	1.106	1.158	1.157	0.712	1.112	1.270	0.889	1.024	2.079	1.164	0.340
	р	0.022	0.035	0.024	0.025	0.019	0.029	0.026	0.024	0.029	0.026	0.026	0.004
	i	0.075	0.088	0.078	0.080	0.037	0.073	0.065	0.081	0.076	0.083	0.074	0.014
	ο	0.016	0.023	0.018	0.020	0.010	0.017	0.017	0.030	0.015	0.046	0.021	0.010
2	n	0.110	0.065	0.052	0.054	0.032	0.073	0.057	0.053	0.049	0.070	0.062	0.020
-	а	1.203	1.485	1.317	1.450	1.067	1.594	1.563	1.220	1.032	1.181	1.311	0.192
	х	0.011	0.012	0.012	0.013	0.011	0.012	0.012	0.012	0.012		0.012	0.000
	u	0.008	0.007	0.265	0.108	0.004	0.038	0.191	0.135	0.297	0.125	0.118	0.102
	Total	1.446	1.716	1.767	1.749	1.181	1.837	1.930	1.555	1.509	1.530	1.622	0.209
	р	0.020	0.024	0.020	0.022	0.014	0.025	0.023	0.019	0.039	0.036	0.024	0.007
	i	0.063	0.098	0.079	0.065	0.037	0.067	0.064	0.096	0.079	0.068	0.072	0.017
3	0	0.012	0.023	0.017	0.020	0.008	0.017	0.015	0.036	0.013	0.027	0.019	0.008
	n	0.130	0.063	0.051	0.056	0.021	0.053	0.056	0.068	0.044	0.068	0.061	0.026
	а	1.935	2.333	1.740	2.202	1.204	2.398	2.329	1.561	1.207	1.737	1.865	0.428
	x	0.011	0.012	0.012	0.012	0.011	0.012	0.012	0.011	0.012		0.012	0.000
	u	0.001	0.018	0.472	0.136	0.000	0.021	0.216	0.286	0.644	0.453	0.225	0.220
	Total	2.173	2.572	2.391	2.512	1.296	2.594	2.715	2.077	2.038	2.388	2.275	0.391
	р	0.024	0.040	0.025	0.028	0.019	0.068	0.028	0.023	0.035	0.028	0.032	0.013
	i	0.065	0.091	0.071	0.063	0.033	0.066	0.062	0.075	0.074	0.070	0.067	0.014
	ο	0.018	0.021	0.022	0.022	0.009	0.022	0.020	0.037	0.016	0.026	0.021	0.007
4	n	0.105	0.053	0.043	0.046	0.030	0.043	0.046	0.044	0.039	0.048	0.050	0.019
	а	1.747	2.088	1.577	1.878	1.269	2.115	1.964	1.395	1.205	1.567	1.680	0.313
	х	0.011	0.012	0.012	0.012	0.010	0.012	0.012	0.012	0.012		0.012	0.001
	u	0.007	0.029	0.367	0.138	0.018	0.100	0.351	0.155	0.411	0.350	0.193	0.152
	Total	1.977	2.333	2.116	2.188	1.389	2.427	2.481	1.740	1.790	2.088	2.053	0.322
	р	0.010	0.015	0.011	0.011	0.008	0.012	0.012	0.010	0.013	0.012	0.011	0.002
	i	0.068	0.089	0.081	0.074	0.044	0.106	0.077	0.081	0.080	0.080	0.078	0.015
	0	0.022	0.016	0.012	0.010	0.004	0.010	0.010	0.011	0.009	0.019	0.012	0.005
5	n	0.034	0.036	0.022	0.049	0.016	0.023	0.026	0.024	0.029	0.025	0.028	0.009
	а	0.709	1.029	0.975	1.011	0.880	1.174	1.123	0.919	0.960	1.016	0.980	0.123
	х	0.013	0.012	0.012	0.013	0.011	0.012	0.012	0.012	0.012		0.012	0.000
	u	0.000	0.005	0.162	0.046	0.000	0.016	0.129	0.032	0.115	0.081	0.059	0.056
	Total	0.856	1.202	1.275	1.213	0.964	1.353	1.389	1.090	1.219	1.232	1.179	0.158

Table 7. Summary of DHA Results by PIONA Group Type, PMI Contributions

Fuel No.	PIONA group	Lab A	LAB B	Lab C	Lab D	Lab E	Lab F	Lab G	Lab H	Lab I	Lab J	Mean	Std. Dev.
	р	0.014	0.020	0.017	0.020	0.019	0.028	0.021	0.017	0.040	0.034	0.023	0.008
	i	0.044	0.074	0.064	0.051	0.034	0.061	0.051	0.069	0.063	0.063	0.057	0.012
	о	0.009	0.016	0.014	0.012	0.009	0.013	0.012	0.021	0.010	0.019	0.014	0.004
60	n	0.079	0.056	0.043	0.041	0.028	0.048	0.046	0.046	0.037	0.049	0.047	0.013
0a	а	1.040	2.083	1.472	1.912	1.281	2.771	1.993	1.202	0.965	1.462	1.618	0.535
	x	0.012	0.013	0.013	0.013	0.012	0.013	0.012	0.012	0.013		0.013	0.001
	u	0.000	0.006	0.464	0.055	0.013	0.032	0.264	0.277	0.563	0.415	0.209	0.205
	Total	1.199	2.268	2.087	2.104	1.395	2.967	2.399	1.644	1.690	2.042	1.979	0.491
	р	0.019	0.019	0.017	0.019		0.030	0.019	0.017	0.040	0.034	0.024	0.008
	i	0.040	0.072	0.063	0.052		0.061	0.051	0.065	0.064	0.061	0.059	0.009
	ο	0.008	0.017	0.013	0.013		0.014	0.011	0.018	0.010	0.017	0.013	0.003
6h	n	0.071	0.057	0.043	0.041		0.054	0.047	0.044	0.038	0.046	0.049	0.010
00	а	1.125	1.971	1.467	1.916		2.747	1.994	1.332	0.982	1.459	1.666	0.515
	х	0.013	0.013	0.013	0.013		0.013	0.012	0.012	0.013		0.013	0.000
	u	0.027	0.003	0.458	0.075		0.043	0.254	0.242	0.600	0.253	0.217	0.194
	Total	1.304	2.152	2.073	2.128		2.963	2.390	1.731	1.747	1.872	2.040	0.441
	р	0.026	0.058	0.028	0.030	0.015	0.038	0.031	0.028	0.031	0.033	0.032	0.011
	i	0.107	0.135	0.120	0.118	0.063	0.132	0.109	0.124	0.111	0.109	0.113	0.019
	ο	0.033	0.027	0.024	0.026	0.010	0.025	0.020	0.031	0.017	0.032	0.024	0.007
7	n	0.116	0.085	0.067	0.067	0.038	0.070	0.072	0.068	0.062	0.083	0.073	0.019
-	а	0.821	1.207	1.011	1.114	0.792	1.310	1.348	0.974	0.832	1.082	1.049	0.190
	х	0.013	0.013	0.012	0.012	0.014	0.013	0.012	0.012	0.012		0.013	0.000
	u	0.130	0.010	0.392	0.190	0.000	0.392	0.314	0.161	0.447	0.204	0.224	0.150
	Total	1.247	1.534	1.654	1.558	0.932	1.981	1.907	1.398	1.512	1.543	1.527	0.286
	р	0.022	0.042	0.021	0.023	0.016	0.044	0.024	0.018	0.037	0.026	0.027	0.009
	i	0.063	0.083	0.072	0.058	0.032	0.066	0.057	0.071	0.072	0.059	0.063	0.013
	0	0.011	0.022	0.017	0.016	0.006	0.017	0.015	0.032	0.012	0.026	0.017	0.007
8	n	0.129	0.055	0.048	0.047	0.017	0.053	0.051	0.052	0.040	0.052	0.054	0.027
	а	1.878	1.826	1.513	1.845	0.965	2.296	1.918	1.065	1.024	1.624	1.595	0.425
	х	0.011	0.014	0.014	0.014	0.012	0.014	0.013	0.013	0.013		0.013	0.001
	u	0.023	0.004	0.447	0.127	0.000	0.132	0.297	0.314	0.547	0.192	0.208	0.180
	Total	2.137	2.044	2.132	2.129	1.048	2.622	2.374	1.565	1.745	1.978	1.978	0.417

Notes: P = n-paraffins; I = i-paraffins; O = olefins; N = naphthenes; A = aromatics, X = oxygenates; U = unidentified Fuels 6a and 6b were replicate samples for all labs except Lab E Shaded cells indicate outlier values

5.2.1 Total Results

An overall statistical summary of the PMI values for each fuel is given in Table 8. The left side of this table shows the mean, standard deviation, and relative standard deviation (RSD) for each fuel when including Lab E; the right side shows values when excluding Lab E. The RSD values declined substantially when Lab E was excluded, except for Fuel 6. As noted above, PMI values for Fuel 6 were rather inconsistent across the labs, with Lab F showing dramatically high values. If Lab F is excluded, the RSD levels for the Fuel 6a and 6b PMI values fall to 19% and 16%, respectively.

				1			
Fuel	I	ncluding Lab E	E	Excluding Lab E			
No.	Mean PMI	Std. Dev.	RSD	Mean PMI	Std. Dev.	RSD	
1*	1.062	0.158	14.9%	1.106	0.104	9.4%	
2	1.622	0.209	12.9%	1.671	0.157	9.4%	
3	2.275	0.391	17.2%	2.384	0.227	9.5%	
4	2.053	0.322	15.7%	2.127	0.247	11.6%	
5	1.179	0.158	13.4%	1.203	0.148	12.3%	
6a	1.979	0.491	24.8%	2.044	0.475	23.3%	
6b				2.040	0.441	21.6%	
7	1.527	0.286	18.7%	1.593	0.217	13.6%	
8	1.978	0.417	21.1%	2.081	0.294	14.1%	

Table 8. Summary of PMI Results for All Fuels

* Fuel 1 results exclude Lab J

The PMI values for each fuel, as measure by each Lab, are shown graphically in Figure 10, where letter symbols are used to indicate the lab identities. The top panel includes Lab E, while the bottom panel excludes this lab. In both panels, horizontal lines are included to indicate the mean value and the 95% confidence interval (CI) for each fuel. This graphical display illustrates that the PMI results for lab E were outside (below) the 95% CI for all fuels (Lab E did not analyze Fuel 6b). After excluding Lab E, Lab A was below the 95% CI for 5 of the 8 fuels, Lab F was above the 95% CI for 5 of the 8 fuels.



Figure 10. Total PMI values by Lab for each fuel. Top includes Lab E; Bottom excludes Lab E. Letter symbols indicate the Lab identities. Horizontal lines represent mean and 95% confidence intervals.

Another way of displaying the total PMI values from each Lab and fuel is shown in Figure 11. In this case, the result from each lab is shown as a fraction of the mean result for all labs. The horizontal blue line in this figure indicates the mean of all 10 labs for each fuel. Letter symbols are used to indicate the identity of each lab. In Figure 11, Lab J's result for Fuel 1 was included, whereas it was

not included in the data shown in Figure 10. This extreme outlier value is attributed to a sample mixup problem, as explained later.

Some labs show inconsistent relative results across the range of fuels. Most noticeable in this regard are Labs F and A. Lab F shows results relatively close to the mean for Fuels 1-5, but considerably higher PMI values than the mean for Fuels 6-8. Lab A shows results close to the mean for Fuels 1-4 and 8, but the results are well below the mean for Fuels 5-7. Possible explanations for these discrepancies are offered in Section 6 (Responses from Participating Laboratories).



Figure 11. Difference in total fuel PMI values from the mean for each lab and fuel. (Letter symbols indicate the Lab identities)

Yet another way to compare these PMI results for all fuels across all labs is shown in Figure 12. In this case, the PMI value of each fuel (identified by numbered symbols) is shown as determined by each laboratory. Some broad consistencies are seen across all labs. For example, Fuel 3 had the highest (or nearly highest) PMI value for all labs, while Fuel 1 had the lowest (or nearly lowest) value for all labs. Also, Fuel 4 was near the highest and Fuel 5 was near the lowest PMI values for all labs. Furthermore, all labs showed that Fuels 2 and 7 had very similar PMI values, which generally lay near the middle of the range of fuels for each lab.

There are also some striking inconsistencies in Figure 12. Most noticeable is Lab E, where PMI values are lower and clustered closer together than with the other labs. This results from Lab E's inability to quantify as many compounds as the other labs. In particular, measurement of heavy components (C_{10+}) was poor by Lab E. These are the species that contribute the most to total PMI.

Another striking inconsistency in Figure 12 is due to Fuel 6. (This was the replicate fuel used by all labs except Lab E.) The replicate analyses were in good agreement for all labs, resulting in the Fuel 6a and Fuel 6b points lying close together for all labs in Figure 12. For most labs, Fuel 6 has about

the 3rd highest PMI value of all the fuels. For Lab F, however, Fuel 6 had the single highest PMI of all fuels (points 6a and 6b lie on top of each other), while for Lab A, Fuel 6 was near the bottom of the PMI ranking.



Figure 12. PMI values of each fuel measured by each laboratory

Figure 13 plots the RSD data from Table 8 against the mean PMI value for each fuel – both including and excluding Lab E. These results suggest that there may be a weak relationship between RSD and PMI, although more data would be necessary to confirm this. It should be pointed out that the two highest RSD values when excluding Lab E came from replicates of the same Fuel 6.



Figure 13. Variability in PMI determination (RSD) vs. PMI level

5.2.2 Results by PIONA Group

Another inter-laboratory comparison was performed by examining the DHA results (both wt.% and PMI contributions) from all laboratories as lumped by PIONA group type. An example of this for Fuel 3 is shown graphically in Figure 14. Similar graphical displays for all fuels are provided in Appendix V. Fuel 3 was chosen to highlight here because it had the highest average PMI value of all the fuels analyzed.



Figure 14. Summary of wt.% (top) and PMI contributions (bottom) by PIONA group from DHA of Fuel 3.

Examining Figure 14 shows some notable differences from lab-to-lab. For example, all labs measured approximately 10 wt.% ethanol (indicated here as group "x"), except Lab J, which did not report ethanol in Fuel 3, or in any other gasoline sample. It seems likely that in most cases, the chromatographic peak resulting from ethanol was categorized by Lab J as an unknown compound. This is supported by the observation that for all fuels shown in Table 6, Lab J has an unidentified wt.% value substantially higher than the average of all labs.

Another significant feature seen in Figure 14 (and all the figures in Appendix V) is that the total amount of unidentified compounds (indicated here as group "u") varied substantially over the 10 laboratories. For most fuels, Labs A, B, D, E, and F reported lower total unidentified compounds

than did Labs C, G, H, I, and J. In general, the higher wt.% of unidentified compounds reported by Labs C, G, H, I, and J translates into an even larger impact of PMI contribution. This results from the fact that most unidentified species are in the heavy ends of the gasoline, which have low vapor pressure and are likely aromatics, and thereby have relatively high PMI values.

While the aromatics category clearly contributes the largest share to total PMI for all fuels, the unidentified category is the second largest contributor in many cases. Particularly with Labs C, G, H, I, and J, the PMI contribution from unidentified compounds exceeds the sum of the contributions from the PION categories with most fuels. It should be remembered, however, that many (perhaps most) compounds classified as unidentified are actually aromatic compounds. Thus, it might be appropriate to combine the unidentified and aromatics categories.

The bottom panel of Figure 14 (and all figures in Appendix V) shows considerable variation in total PMI values among the 10 labs. The horizontal red line in this figure represents the mean value of 2.275. With Fuel 3, Lab G has the highest PMI value (2.715) and Lab E has the lowest (1.296), with the difference between them being a factor of two. Mean PMI values for all the fuels, along with standard deviations, are shown in Table 8 – with and without including Lab E.

5.2.3 Detailed Results of Aromatics

Because the overall PMI value for a given fuel is driven largely by the fuel's aromatic components, additional analyses were conducted to examine the aromatics in more detail. One analysis is shown in Figure 15, where the wt.% and PMI contributions of the aromatics are shown, by carbon number, for Fuel 3, as determined by all 10 laboratories. Appendix VI provides similar figures for all the fuels analyzed.

Figure 15 reveals several interesting features. First, the total wt.% of aromatics (top panel) in these fuels is dominated by light aromatics, primarily C_7 - C_9 constituents, whereas the total PMI contributions (bottom panel) are dominated by heavier aromatics, primarily C_{10} - C_{12} constituents. Second, for a given fuel, the range of wt.% values across the set of laboratories is approximately the same at all carbon numbers, whereas the range of PMI values is much larger for the heavier aromatics compared to the lighter aromatics. This expansion of the PMI range with carbon number is largely due to reductions in vapor pressure – and hence increases in PMI factor – that occur with heavier compounds (see Equation 1). Third, the measurement of heavy aromatics (and probably other heavy species) appears to be more difficult for some labs than for others. Lab E in particular gave low wt.% values for C_{10+} aromatics in all fuels. This largely explains the overall low PMI results for Lab E shown in Figure 11 and Figure 12.

Another point to be made about Figure 15 is that while Lab E shows low results for the heavy aromatics (C_{10+}), and hence low PMI values, it shows high values for light aromatics (C_6 - C_9). This is a consequence of Lab E (and all other labs) reporting their results as wt.% of total, normalized to 100%. Because of this methodology, inability to detect heavy species (aromatics or others) results in overestimation of lighter species.



Figure 15. Wt.% (top) and PMI contribution (bottom) of aromatic constituents by carbon number for Fuel 3 (Letter symbols indicate the Lab identities)

These aromatics results for all fuels are presented in a different way in Appendix VII, where the wt.% and PMI contributions are shown in bar graph form, by laboratory. Additionally, bar segments are used to show the results by carbon number. An example, for Fuel 3, is included here as Figure 16. The red horizontal lines included in these figures indicate the mean values across all labs. As seen in Appendix VII, Lab E's wt.% aromatics results were higher than the mean, while its PMI results were



lower than the man – for every fuel. This is a consequence of under-reporting heavy aromatics and over-reporting light aromatics.

Figure 16. Wt.% (top) and PMI contribution (bottom) of aromatic constituents by Laboratory for Fuel 3 (Colored bar segments indicate carbon number. Horizontal line indicates mean of all Labs.)

5.2.4 Results of Individual Compounds

Figure 17 shows the wt.% of each named species measured by each lab, relative to the mean value measured by all labs (excluding Lab E) for Fuel 3. The species are ordered by retention index on the x-axis. A color scale is used to indicate the concentration of each component, with blue and violet being low concentration species (<0.1 wt.%), while green and yellow indicate high concentration

species (>1.0 wt.%). Lab E is excluded from this analysis because in many cases, its results would significantly distort the mean values, thus causing other lab's results to differ from the mean by larger amounts.

Examination of Figure 17 shows that most data points from each lab are distributed fairly evenly around the mean values, indicated by the horizontal red line. However, most labs also show a small number of outlier points. It may be useful to investigate the identities of these outliers, and determine whether they result from compound mis-identification or other chromatographic problem, but to do so here is outside the scope of this project.



Figure 17. Relative wt.% of each named component measured in Fuel 3 by each lab. (Horizontal line indicates the mean of all labs. Lab E was excluded from this analysis.)

Similar graphical displays for all the fuels are provided in Appendix VIII. These figures generally resemble that shown for Fuel 3 in Figure 17, but with a few notable exceptions. Particularly

significant is the apparent volatility bias seen in the results from some fuels by Lab F. For most labs and most fuels, no volatility bias is seen, meaning that the datapoints are generally evenly distributed around the mean across the entire range of RI values. This even distribution is Also seen in Lab F results for Fuels 1, 2, 3, and 4. However, for Fuels 5-8, a noticeable bias is evident, with the concentration of high volatility species (low RI values) being below the mean and the concentration of low volatility species (high RI values) being above the mean. A likely explanation for this behavior is evaporative loss of the gasoline samples prior to injection into the GC instrument. Such evaporative loss would preferentially reduce the concentration of light constituents, thereby increasing the concentration of heavier constituents, when expressed on a wt.% basis. Lab F later confirmed that they identified sample volatility losses associated with residence time in the chromatograph's autosampler prior to injection. As described later (Section 6), re-analysis of these samples after correcting this volatility loss problem largely resolved the bias.

The volatility bias seen in Lab F also impacts calculated PMI values. The light end constituents lost through evaporation have very low PMI values, whereas the enriched heavy constituents have higher PMI values. Thus, an evaporative loss problem would lead to PMI results that are biased high. This can be seen in Figure 10 and Figure 11, where the PMI results from Lab F are close to the mean for Fuels 1-5, but are well above the mean for Fuels 6-8.

A somewhat similar volatility bias (but with an opposite sign) appears in the results from Lab A. In this case, the more volatile constituents measured are above the mean levels, while the low volatility constituents are below the means. This suggests a calibration problem, or perhaps a situation whereby the chromatographic peaks from the late-eluting, heavy compounds are not being integrated properly. We also note that Lab A was one of only three labs (the others being Lab G and Lab I) that did not begin their chromatographic analysis under cryogenic conditions, although it is unclear whether this is related to the volatility bias problem. In response to additional questions asked of the Labs after all the data were collected (see Appendix XI), Lab A reported that an incorrect GC inlet liner (splitless instead of split) was used for these analyses. This may have been responsible for the apparent volatility bias in the data.

Another striking feature of the individual lab results shown in Appendix VIII is the anomalously poor agreement with the mean by Lab J for Fuel 1. The scatterplot results shown in Appendix VIII-1 suggests that a sample mix-up occurred. Upon closer inspection, it appears that rather than Fuel 1, the sample being analyzed was really Fuel 6. This can be seen by inspection of Figure 18, which shows DHA results reported by Lab J for both Fuel 1 (blue circle points) and Fuel 6 (red x points). The blue and red points lie nearly on top of each other for every component, suggesting that these two fuels being shown are actually identical. (The lines connecting the points in Figure 18 are used as a visual aid, creating the appearance of a chromatogram, but they have no physical meaning.) Also shown in Figure 18 (as green squares) are the DHA results for Fuel 1 as reported by Lab A. (Fuel 1 results from all other labs besides Lab J are similar to those shown here for Lab A.) The green points in Figure 18 are clearly different from the red and blue points, confirming that Lab J did not actually analyze and report results for Fuel 1. (Note: the possibility of a mix-up during DRI's sample preparation and shipping cannot be ruled out, although this seems unlikely.)



Figure 18. DHA wt.% results for Fuel 1 and Fuel 6 by Lab J, and Fuel 1 by Lab A.

While it is clear that as a group, aromatics contribute the largest share of a fuel's total PMI value, it is also of interest to investigate the contributions of individual components. An attempt to do this is illustrated in Figure 19, which shows the PMI contributions of the top 50 species in Fuel 3 and Fuel 5 as reported by Lab D. Similar figures for all the labs are included in Appendix IX. Fuels 3 and 5 were selected for these analyses because they represent the extremes in terms of total PMI levels. As shown in Table 8, Fuel 3 has the highest average PMI of the 8 test fuels (value of 2.28) while Fuel 5 has nearly the lowest PMI (value of 1.18). Fuel 1 has an even lower PMI value of 1.06, but this fuel was not analyzed by Lab J.

Figure 19 shows that the largest single PMI contributor in Fuel 3 is 2-methylnaphthalene. All top 50 contributors in Fuel 3 are aromatic species, except for ethanol. Most of the PMI contribution beyond the top 50 components also comes from aromatic species, as seen by the large "Remainder of A" bar. A small fraction of the total PMI is attributed to unidentified compounds (see blue "Remainder of U" bar), with relatively little contributions from the other PIONA group types.

As shown in Figure 19, Fuel 5 has a very different list of top 50 contributors, with the top two being m-xylene and toluene. 2-Methylnaphthalene, which is the top contributor in Fuel 3, is the 12th largest contributor in Fuel 5. Eight of the top 50 contributors in Fuel 5 are not aromatics, with the largest one being identified as isopropylcyclobutane – number 10 out of 50. [Note: this species is not explicitly named in the compound list of the standard ASTM D6730 method, but is one of many species added to the database by SSI as part of CRC Project AVFL-29. Thus, it appears in the Appendix 1 compound list of ASTM D6730.] Based on our understanding of petroleum-derived fuels, it seems unlikely that a cyclobutane compound would be present in such abundance. Additional work is required to confirm or deny this designation.

Examination of all the figures in Appendix IX reveals several interesting features. With all labs, the total fuel PMI was dominated by the contribution of aromatics. This was especially true with Fuel 3 (a relatively heavy fuel) as compared to Fuel 5 (a relatively light fuel). With most labs, nearly all the top 50 contributors in Fuel 3 are aromatics, whereas a handful of non-aromatic contributors appeared in the top 50 list for Fuel 5. Lab E showed very different distributions from the rest of the labs – for both fuels. This is a consequence of the much smaller number of identified components reported by Lab E. With some labs, a significant fraction of the total PMI was attributed to unidentified species. This was especially the case for Labs C, H, I, and J. Labs D and G showed a modest contribution of unidentified components, while Labs A, B, E, and F showed little to none.

For 7 of the 10 labs, the largest single contributor to PMI of Fuel 3 was 2-methylnaphthalene. The exceptions were Lab A (1-methylnaphthalene), Lab E (1,2,4-trimethylbenzene) and Lab I (1,2,4-trimethylbenzene). For Fuel 5, all labs showed major contributions to total PMI from toluene, ethylbenzene, xylenes (TEX) in addition to 1,2,4-trimethylbenzene. Lab G was an exception in showing an additional component, a C_{15+} unidentified species, in the top 3.



Figure 19. Top 50 individual contributors to total PMI of Fuels 3 and 5, determined by Lab D

It is also of interest to examine how the labs performed with respect to a few, known co-elution challenges. Method ASTM D6730 identifies a number of compound pairs for which co-elution can be a problem. Six of these pairs are shown below in Table 9. Problems with chromatographic resolution of these compound pairs also could affect the calculated PMI of the fuel, as the PMI factors for some pairs differ substantially. [Note: the PMI factors shown in Table 9 were taken from the SSI database from CRC Project AVFL-29.]

Pair No.	Possible Co-Eluting Compounds	Group Type	PMI Factors x 10 ³
1	ethanol / 3-methylbutene-1	oxygenate / olefin	1.17 / 0.64
2	2,3-dimethylbutane / methyl-t-butyl ether	i-paraffin / oxygenate	0.75 / 0.70
3	1-methylcyclopentene / benzene	naphthene / aromatic	3.50 / 6.07
4	2,3,3-trimethylpentane / toluene	i-paraffin / aromatic	2.66 / 12.1
5	p-xylene / 2,3-dimethylheptane	aromatic / i-paraffin	23.8 / 4.86
6	1-methylnaphthalene / tridecane	aromatic / n-paraffin	515 / 55.7

Table 9. Potential Co-Elution Problems Identified in ASTM D6730

Figure 20 displays the concentration results for each of these pairs of compounds measured by each lab in every fuel, expressed relative to the mean results from all labs. A few outlier points seen in this figure suggest the possibility that some labs had difficulty in resolving some of the closely eluting compounds. Considering Pair 1, for example, Lab J showed exceptionally high values of 3-methylbutene-1 in Fuels 2 and 8 (note the scale change for these fuels), while no ethanol was reported. (In fact, Lab J did not report ethanol in any of the fuels.) This suggests that some fraction of the large chromatographic peak resulting from ethanol was mistakenly attributed to 3-methylbutene-1, thus giving an exaggerated result for this compound. Though less severe, the same problem may have occurred with Lab I when analyzing Fuels 1, 3, 4, 5, 6, and 7. The PMI consequences of misidentifying ethanol and 3-methylbutene-1 are not very large, as the PMI factors for these two compounds differ by less than a factor of 2.

Pair 2 appeared to cause no problems, as methyl-t-butyl ether (MTBE) was not present in any of these fuels. Pair 3 also appeared to cause no problems. With Pair 4, however, Lab I reported very low results for 2,3,3-trimethylpentane in Fuel 6 (both a and b), although a correspondingly high concentration of toluene was not seen. However, these two fuel components are present at very different concentrations, with toluene being much more abundant. It is possible to mis-appropriate some of the peak area due to 2,3,3-trimethylpentane as being part of the toluene peak, without dramatically changing the reported concentration of toluene. Confusion of these two compounds in Pair 4 could have some PMI impacts, as the PMI factors for these species vary by a factor of 4.5.



Figure 20. Wt.% results of potential co-eluting compound pairs by each lab, relative to mean results of all labs.

With Pair 5, Lab D reported noticeably higher concentrations of 2,3-dimethylheptane than the mean of all labs. The fact that this is not countered by lower than mean values for p-xylene may be due to the much higher abundance of p-xylene. Finally, Pair 6 illustrates several interesting features. For most fuels, Lab I shows high results for tridecane and low results for 1-methylnaphthalene, suggesting that a chromatographic resolution problem may have existed. Lab J shows similar behavior, but only in a few of the fuels (Fuels 3, 6a, and 6b). Lab A shows the opposite behavior, with high values for 1-methylnaphthalene and low values for tridecane in most fuels. Although these Pair 6 compounds have PMI factors that differ by a factor of 9, mis-identification of them would likely have only a small effect on the fuel's total PMI because of their extremely low abundance.

In the figures of Appendix VIII, showing comparisons of individual lab's results to mean results for all named compounds, there is evidence of volatility bias for some labs and fuels. By this we mean that the results from a particular lab may agree well with the means for compounds within a particular range of RI values, but agree poorly with the means of compounds in other RI ranges. The clearest example of this is Lab F with Fuels 6a and 6b.

To examine this issue more closely, Figure 21 shows the wt.% results for n-paraffins by carbon number (C_3 - C_{16}) of each lab compared to the mean of all labs. As expected, inter-laboratory variability is lowest in the mid-carbon range (C_6 - C_{10}) where the components are present in highest abundance, and increases for both lower and higher carbon components. The aforementioned volatility bias of Lab F with Fuels 6a and 6b is seen clearly in Figure 21, as is an opposite bias of Lab A with several fuels. Also of note is Lab I's generally high results for C_{13} and C_{14} n-paraffins. Because these high results of Lab I are not compensated by low results for the low carbon species, this does not represent a volatility bias like that seen for Lab F.

The general pattern observed in Figure 21 of tightly clustered data points for C_6 - C_{10} and greater data spread for larger and smaller carbon number ranges is consistent with the repeatability and reproducibility of DHA determination as reported in Table 4 of ASTM D6730. In this table, reproducibility of C_6 , C_7 , C_8 , C_9 , and C_{10} n-paraffins are reported to be 5.1%, 10.8%, 15.7%, 10.3%, and 17.9%, respectively. Reproducibility of C_4 , C_5 , C_{11} , and C_{12} n-paraffins are reported to be 32.4%, 10.4%, 40.0%, and 32.9%, respectively. Although thorough analysis of repeatability and reproducibility is beyond the scope of this project, the n-paraffin results shown in Figure 21 seem broadly consistent with the values reported in ASTM D6730.

Finally, in an effort to identify specific compounds that an individual lab consistently measures much higher or lower than other labs, a series of "tick mark graphs," such as that shown in Figure 22 for Lab D, were prepared and are included in Appendix X. The positive and negative tick marks represent individual compounds that are measured at concentrations higher or lower than the mean of all labs by a factor of 4 or greater. Only compounds measured by at least 5 labs are included, and all results from Lab E are excluded from these analyses. Additionally, the tick marks are color coded to indicate the PIONA group type, and are arranged along the x-axis by RI value. (This is called "approximate RI" because the exact RI for a given compound changes slightly from sample-to-sample.)



Figure 21. Wt.% results of n-paraffins by each lab, relative to the mean of all labs



Figure 22. Lab D wt.% results showing compounds with large deviations from all lab means

One thing to note in Figure 22 (and in all Appendix X figures) is that there are far more negative tick marks than positive marks. This results from the arbitrary method used in setting the thresholds to define a "large deviation" from the mean. Because of typical data clustering among the labs, it is more common to have a value below one-quarter of the mean than it is to have a value 4 times the mean. Adjusting these threshold limits could be done to include a greater or lesser number of tick marks.

It was initially thought that these tick mark figures might provide a unique "fingerprint" for each lab, identifying where a particular lab is consistently high or consistently low. However, due to lack of consistency from fuel-to-fuel, useful fingerprints are not apparent from these figures. Nevertheless, some interesting features are seen, which the participating laboratories may want to explore further. A few examples from each lab are mentioned below.

- Lab A: High i-paraffin near RI of 410 (2 of 9 fuels) Low olefin near RI of 710 (5 of 9 fuels) Low aromatic near RI of 1100 (7 of 9 fuels)
- Lab B: Low olefin near RI of 500 (7 of 9 fuels) Low olefin near RI of 520 (6 of 9 fuels) Low naphthene near RI of 720 (9 of 9 fuels) Low i-paraffin near RI of 880 (8 of 9 fuels)
- Lab C: Low olefin near RI of 500 (7 of 9 fuels) Low naphthene near RI of 715 (6 of 9 fuels) Low i-paraffin near RI of 820 (9 of 9 fuels) Low i-paraffin near RI of 870 (8 of 9 fuels) Low aromatics near RI of 1040 (6 of 9 fuels)
- Lab D: Low olefin near RI of 510 (7 of 9 fuels) Low naphthene near RI of 820 (8 of 9 fuels) Low i-paraffin near RI of 950 (6 of 9 fuels)
- Lab F: Low olefin near RI of 500 (7 of 9 fuels) Low naphthene near RI of 710 (6 of 9 fuels) Low naphthene near RI of 820 (5 of 9 fuels)
- Lab G: Low olefin near RI of 510 (5 of 9 fuels) Low naphthene near RI of 530 (5 of 9 fuels) Low olefin near RI of 700 (8 of 9 fuels) Low i-paraffin near RI of 930 (7 of 9 fuels)
- Lab H: High olefin near RI of 500 (6 of 9 fuels) Hi olefin near RI of 510 (6 of 9 fuels) Low aromatics near RI of 1040 (4 of 9 fuels)
- Lab I: Low olefin near RI of 500 (6 of 9 fuels) High naphthene near RI of 780 (4 of 9 fuels) Low i-paraffin near RI of 840 (9 of 9 fuels) High i-paraffin near RI of 950 (8 of 9 fuels) Low aromatics near RI of 1060 (7 of 9 fuels) Low aromatics near RI of 1110 (8 of 9 fuels) Low naphthene near RI of 1140 (7 of 9 fuels) Low aromatics near RI of 1170 (9 of 9 fuels) Low aromatics near RI of 11300 (6 of 9 fuels)
- Lab J: Low olefin near RI of 510 (5 of 8 fuels) High naphthene near RI of 710 (6 of 8 fuels) Low naphthene near RI of 780 (8 of 8 fuels) Low i-paraffin near RI of 930 (7 of 8 fuels) Low aromatics near RI of 1100 (4 of 8 fuels)

6. Responses from Participating Laboratories

Following data analysis and preparation of a draft final report, CRC agreed to distribute the report to all laboratory participants, with a request to review and comment on particular aspects. A list of eight questions was distributed to all the labs. These questions, along with answers from the five labs who responded, are documented in Appendix XI.

Several of the reporting laboratories provided greater detail on the initial Laboratory Questionnaire that had been requested several months earlier. This additional information was used to update the summary of responses shown in Table 3 of this report. Some responses provided clarification of analytical methodologies (e.g., QC measures taken, thresholds for peak identification, and treatment of ethanol), while other responses addressed specific cases where a Lab's result was called out as being an outlier. Although these responses provided additional insights into several of the Lab's methodologies and limitations, they did not affect overall data interpretation or conclusions drawn from this study.

In their response, Lab A commented that some adjustments went into the data set as "The total naphthenes and total olefins don't match what we reported. It looks like the naphtheno-olefin values may have been added into the naphthenes …" This is a good point. It is worth noting that the compound lists in ASTM D6730 do not include PIONA classifications for the compounds. Thus, there can be confusion and disagreement about classification of some species – such as certain olefins and naptheno-olefins.

In addition to the eight questions mentioned above, Lab A was asked to address a volatility bias that was apparent in the results from some of the fuels. As shown in the figures of Appendix VIII, this was especially noticeable in results from Fuels 5, 6, and 7, where light fuel constituents appeared to be over-estimated and heavy constituents were under-estimated, compared to the means of all labs. Lab A explained that a splitless GC inlet liner had mistakenly been used instead of a liner meant for split injections. It is likely that this was at least partially responsible for the apparent volatility bias.

Finally, Lab F was asked to explain the apparent volatility bias that existed in their results from some (but not all) fuels. Two of the most extreme examples of this are Fuels 6a and 6b, as shown in the Figures of Appendix VIII. These figures suggest that loss of gasoline light ends may have occurred, resulting in over-estimation of heavier constituents, and hence, over-estimation of the fuel's PMI values. Lab F confirmed that some of the gasoline samples had sat in the GC's autosampler for an extended period (several hours) prior to injection and analysis. This warm environment, perhaps combined with improperly sealed autosampler vial inserts, may have led to evaporative losses of gasoline. To investigate this possibility, Lab F re-analyzed Fuels 6a and 6b, while taking precautions to keep the samples cool and avoid any sample leakage. Results from both the initial analysis and re-analysis are shown in Figure 23. It is apparent that with these additional precautions, loss of gasoline light ends was reduced, though not completely eliminated. As a result of this re-analysis, the calculated PMI values for these fuels were reduced, bringing them closer to the mean values for all labs, as shown in Figure 24.





Original analyses (from all labs) are shown in Appendix VIII-6 (Fuel 6a) and Appendix VIII-7 (Fuel 6b)



Figure 24. PMI of Fuels 6a and 6b from DHA measurements by Lab F: before (old) and after (new) modifying sample handling procedures to minimize evaporative loss.

7. Summary and Conclusions

In this project, 10 participating laboratories performed DHA determinations on a set of 8 gasolines. No specific analytical method was required; instead the labs were asked to use whatever method they usually employ for such fuel characterization. Based on information obtained from a laboratory questionnaire, it was learned that the labs utilized variations of at least three different methods: ASTM D6729, ASTM D6730, and a recently-developed extended version of ASTM D6730.

Analytical results from each laboratory, in units of wt.% for each measured component, were submitted to DRI in whatever electronic format that lab typically uses. Results from all labs were combined into a single, uniform database for use in subsequent data analysis. A common compound naming convention was developed, using the Master List of compounds recently defined by SSI in the previous CRC Project AVFL-29 as a starting point. PMI factors for explicitly-named compounds were also taken from the SSI Master List. For generically-named and un-named compounds, PMI factors were determined from regression data of PMI vs. retention index (RI) for the 822 compounds in the SSI Master List.

Unknown to the participating labs, duplicate samples of one of the eight fuels was included, thus providing a basis to assess intra-laboratory variability. Despite a few outlier points, the wt.% results for individual compounds measured in these replicate samples showed overall excellent agreement for all labs. This provides confidence that a given lab is able to repeatably determine the PMI value of a given fuel.

Total PMI values were calculated for each fuel by applying the common set of PMI factors to the DHA wt.% results from each laboratory. Although PMI values for a given fuel varied substantially from lab-to-lab, the general ranking of fuels from high to low PMI was quite consistent across all labs. This provides confidence that in previous studies investigating the effects of a range of fuels on PM emissions, the relative rankings of the fuels' PMI values were probably correct, even if the exact numbers are uncertain.

The overall inter-laboratory fuel PMI variability observed in this study [expressed as relative standard deviation (RSD)] ranged from about 10% to 20% across the eight fuels. Of the PIONA hydrocarbon group types, aromatics were the dominant contributors to total PMI of all the fuels. In 7 of the 8 fuels, aromatics comprised 22-33% of the fuel mass, but were responsible for 76-83% of the total calculated PMI values. The 8th fuel was lower in aromatics (17%), but the aromatic species were still responsible for 69% of the total fuel PMI. In many cases, the second largest contributors to total PMI were unidentified components, most of which were likely aromatics. Thus, for some analyses, it may be appropriate to combine the unidentified and aromatics categories.

Further examination of the fuel aromatics by carbon number showed that in most fuels, mass contributions were greatest in the C_7 - C_9 range, while PMI contributions were greatest in the C_{10} - C_{12} range. It appears that a significant contributor to overall inter-laboratory PMI variability is inconsistent measurement of C_{10} - C_{12} aromatics by the different laboratories. While even heavier aromatics (C_{13+}) have larger PMI impacts per mass, these species are present in such low abundance that they do not significantly affect a fuel's total PMI value.

Analysis of selected individual compounds indicated that the potential co-elution situations identified in ASTM D6730 were not major problems in this project. Analysis of a broader range of individual compounds revealed several significant data problems, which if uncorrected, could adversely affect inter-laboratory variability. One laboratory measured far fewer compounds than the other 9 labs (particularly fewer heavy aromatics), resulting in calculation of considerably lower PMI values. One laboratory had a sample mis-identification problem, whereby the results from one fuel were attributed to a different fuel. One laboratory appeared to have a sample integrity problem, whereby evaporative loss of gasoline light ends (in some fuels) caused an over-estimation of heavy constituents, resulting in a high bias for PMI values.

Detailed information about the analytical methods used by each lab was obtained from a questionnaire, which indicated that many variations of standard ASTM methods were used. Based on the results obtained in this study, it is not possible to define one method as being superior to the others, with respect to PMI determination. Nevertheless, a method that quantifies a larger number of compounds (especially C₁₀-C₁₂ aromatics) would be preferred over one that quantifies a smaller number of compounds. For this reason, use of the extended ASTM D6730 method would be preferred over the standard method. Also, a method that attributes PMI contribution to unidentified compounds is preferred over a method that ignores these compounds.

8. Recommendations

In this inter-laboratory study, participating labs were asked to conduct DHA analyses on a set of gasoline samples using whatever analytical methodology they normally employ. The resulting fuel PMI values calculated from these DHA results showed relatively high inter-laboratory variability, with RSD values in the range of 10-20% across the eight fuels. If further intercomparison studies are contemplated, it is recommended that all participating labs be asked to perform the same (or very similar) analytical method. The newly-developed extended version of ASTM D6730 would be preferred, as it contains a much more complete list of identified compounds in gasoline samples. However, this compound list, which appears as Appendix Table X1.2 in ASTM D6730, does not include a PIONA group type designation for each component. Such designations should be made. Also, because total PMI values are dominated by the contribution of heavy aromatic species, future intercomparison studies should focus on these compounds – particularly C_{10} - C_{12} aromatics.

The contribution of unidentified compounds to a gasoline's total PMI value can be quite significant, and should not be ignored. Use of the extended ASTM D6730 method, with the more extensive compound list included in Appendix 1, would likely result in a fewer number of unidentified species as compared to the normal ASTM D6730 method. At present, there is no widely accepted method for assigning PMI factors to unidentified compounds. This issue should be investigated to establish a consensus on how to treat unidentified compounds for purposes of PMI determination.

Because ethanol comprises a large fraction of most gasolines, it can have a significant impact on the final calculated PMI of a particular fuel. A consistent means of treating ethanol within various DHA methods should be used. At a minimum, each chromatogram should be inspected to confirm proper identification of the ethanol peak, ensure that the baseline is drawn correctly, and confirm that integration start and stop times are correct. Also, it is critical to apply an appropriate detector

response factor for ethanol, which is likely very different from the response factors of most hydrocarbon species.

The equation used to define a fuel's PMI value includes the vapor pressure of each fuel constituent. Because vapor pressure decreases drastically as molecular weight increases, the contribution of heavy gasoline species (C_{12+}), regardless of PIONA group type, has a disproportionate influence on the total PMI value. It may be worthwhile investigating the accuracy of vapor pressure values attributed to these heavy species in gasoline.

Finally, it is recommended that greater attention be paid to sample handling procedures – particularly with respect to conditions that could lead to evaporative loss of gasoline light ends. Use of small volume inserts within autosampler vials should be avoided, as they can cause problems with inadequate sealing. Additionally, precautions should be taken to avoid long wait times and warm temperatures within the GC autosampler before the gasoline samples are injected into the instrument.

The standard basis for reporting DHA results is as wt.% for each component, normalized to 100% for all components. On this basis, loss of gasoline light ends results in over-reporting of heavier constituents, causing an over-estimation of the fuel's PMI value. To determine whether this problem is occurring (at least within an interlaboratory comparison program), it would be useful to report directly measured concentration values (in units of mg/mL or mg/g) of key indicator species within the fuel.

9. References

- 1 Khalek, I., T. Bougher, and J. J. Jetter; Particle Emissions From a 2009 Gasoline Direct Injection Engine Using Different Commercially Available Fuels. *SAE Technical Paper*, 2010-01-2117, 2010.
- 2 Leach, F., E. Chapman, J.J. Jetter, L. Rubino, E.D. Christensen, P.C. St.John, G.M. Fioroni, and R.L. McCormick; A Review and Perspective on Particulate Matter Indices Linking Fuel Composition to Particulate Emissions from Gasoline Engines. *SAE Int. J. Fuels and Lubricants* 15 (1) 1-26, 2022.
- 3 Fatouraie, M., M. Frommherz, M. Mosburger, E. Chapman, S. Li, R. McCormick, and G. Fioroni; Investigation of the Impact of Fuel Properties on Particulate Number Emission of a Modern Gasoline Direct Injection Engine. *SAE International* 2018-01-0358, 1-14. 2018.
- 4 Stein, R. A., J. E. Anderson, and T. J. Wallington; An Overview of the Effects of Ethanol-Gasoline Blends on SI Engine Performance, Fuel Efficiency, and Emissions. *SAE Int. J. Engines*, 6, (1), 470-487. 2013.
- 5 Yao, C., Z. Dou, B. Wang, M. Liu, H. Lu, J. Feng, and L. Feng; Experimental Study of the Effect of Heavy Aromatics on the Characteristics of Combustion and Ultrafine Particle in DISI Engine. *Fuel* 203, 290-297. 2017.
- 6 Raza, M., L. Chen, F. Leach, and S. Ding; A Review of Particulate Number (PN) Emissions from Gasoline Direct Injection (GDI) Engines and Their Control Techniques. *Energies* 2018, 11, 1417. 2018.

- 7 Aikawa, K., T. Sakurai, and J. J. Jetter; Development of a Predictive Model for Gasoline Vehicle Particulate Matter Emissions. *SAE Int. J. Fuels Lubr.*, 3, (2), 610-622. 2010.
- 8 Aikawa, K. and J. J. Jetter; Impact of Gasoline Composition on Particulate Matter Emissions From a Direct-Injection Gasoline Engine: Applicability of the Particulate Matter Index. *International J of Engine Research*, 15, (3), 298-306. 2014.
- 9 Leach, F., R. Stone, and D. Richardson; The Influence of Fuel Properties on Particulate Number Emissions From a Direct Injection Spark Ignition Engine. *SAE International*, 2013-01-1558, 1-10. 2013.
- 10 Chapman, E., M. Winston-Galant, P. Geng, R. Latigo, and A. Boehman; Alternative Fuel Property Correlations to the Honda Particulate Matter Index (PMI). *SAE International* 2016-01-2250, 1-8. 2016
- 11 ASTM International; Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100 Metre Capillary High Resolution Gas Chromatography. Designation: D6729-14, 1-51. 2016.
- 12 ASTM International; Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100-Metre Capillary (with Precolumn) High-Resolution Gas Chromatography. Designation: D6730-01, 1-55. 2016.
- 13 ASTM International; Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 50-Metre Capillary High Resolution Gas Chromatography1. Designation: D6733-01 (Reapproved 2011), 1-23. 2011.
- 14 Enhanced Speciation of Gasoline, Final Report for CRC Project AVFL-29. Coordinating Research Council, Alpharetta, GA. June 2018.
- 15 Wikipedia page on Outlier: https://en.wikipedia.org/wiki/Outlier.