

Assessment and Optimization of  
ASTM D7096 Simulated Distillation  
for Quantifying Heavy Hydrocarbons  
in Gasoline

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Assessment and Standards Division  
Office of Transportation and Air Quality  
U.S. Environmental Protection Agency

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## 1. Executive Summary

Multiple studies have shown that the chemical makeup of gasoline has a major influence on combustion-related particulate matter (PM) emissions from vehicles, and that combustion of heavy aromatic compounds in particular is a major PM contributor [3, 4, 5, 6, 7]. An analysis of a large sample of US market gasolines has shown that the high-boiling tail contains a large fraction of aromatics; for example, the heaviest 10 v% is over 80% aromatics [12].

ASTM D7096 SimDis is a gas-chromatography method that can provide a relatively precise volatility profile of a gasoline sample. Given the highly aromatic makeup of the tail of typical gasoline, quantification of high-boiling material by SimDis may provide a good surrogate for more rigorous PM predictors such as PM Index.

The present work explored sources of variability in SimDis results and developed several procedural recommendations to improve repeatability and reproducibility within the method as written, focusing on the high-boiling (T90+) tail of gasoline. Validation studies done at EPA and GM laboratories showed that reproducibility values well below those published by ASTM can be achieved.

Following the method improvement work, SimDis as well as ASTM D6730 DHA were run on 80 gasoline samples taken from the US market in 2021-22. The contribution to PM Index and volume percent was assessed by boiling range and molecular class. This analysis shows that the heavy tail of gasoline contains a large proportion of aromatics that have high leverage on PM Index, findings that are consistent with previous work [12]. The correlation between PM Index values and a range of heavy-end SimDis T-numbers (%-off fractions) was also assessed. Results indicated that the highest correlation occurred in the range of SimDis T95-T98 with a Pearson coefficient of around 0.83.

Finally, the impact on PM Index of applying several SimDis endpoint limits to trim heavy-end material from market gasoline was assessed. Starting from the survey sample average PMI of 1.6, this analysis suggests a PMI reduction of about 0.5 (31%) could be achieved by applying a SimDis endpoint limit of 430°F. This would correspond to removing the heaviest 1.7 v% of an average market fuel, and supports the conclusion that a relatively large reduction in PM Index could be achieved by trimming a small amount of high-boiling material from gasoline.

## 2. Introduction / Purpose

### 2.1. Background

Particulate matter (PM) pollution has been linked to a multitude of health problems [1, 2]. Particles smaller than 2.5 micrometers in diameter, referred to as PM<sub>2.5</sub>, pose the greatest risk because they can penetrate deep into the lungs and enter the bloodstream. Exposure to PM<sub>2.5</sub> increases the risk of premature death and can impair lung growth in children. For individuals with preexisting health challenges, PM<sub>2.5</sub> can increase the risk of cardiovascular and respiratory disease. The United States Environmental Protection Agency (US EPA)'s 2017 National Emissions Inventory estimates that gasoline-fueled vehicles and nonroad equipment contribute 31.9% of the total mobile source primary PM<sub>2.5</sub> emissions [1].

Multiple studies have shown that the chemical makeup of gasoline has a major influence on combustion-related PM emissions [3, 4, 5, 6, 7]. Combustion of heavy aromatic compounds in particular is a major PM contributor. The heavy end of gasoline consists almost exclusively of aromatics, and the heaviest several percent of those species have a disproportionately large impact on the amount of PM emitted.

Advancements continue in engine and aftertreatment technology to mitigate PM emissions. However, these improvements only affect new products. Over 250 million gasoline-powered on-road vehicles and about 150 million nonroad vehicles and pieces of equipment exist in the United States [8, 9], with many of them expected to remain in use for decades to come. Changes in fuel composition can affect this entire population of equipment, resulting in an immediate air-quality benefit.

### 2.2. Motivation for Assessment and Validation of Simulated Distillation Method

A number of test methods are available for assessing properties of gasoline that correlate with PM emissions, but each leaves room for improvement [10, 11]. Quantifying heavy aromatics (e.g., with molecular size of ten carbons and above) would be ideal but getting this level of detail for a fuel sample requires results from a relatively rigorous method. One such method is detailed hydrocarbon analysis (DHA) by ASTM D6730. This method runs for 2-3 hours and produces a chromatogram that must be interpreted by an experienced analyst, making it difficult to standardize and automate. Calculations using data from DHA form the basis of the PM Index, which has been shown to be directly proportional to tailpipe PM emissions [4, 6].

Distillation by ASTM D86 has been part of market gasoline standards for decades, and therefore the equipment and expertise to run the method are widespread. However, correlation of distillation points such as T80 or T90 with heavy aromatic content, a key driver of PM emissions, is only mediocre. A comparison of D86 results with those of DHA illustrate that D86 does a relatively poor job of separating compounds by volatility and underestimates the final boiling point significantly [12]. These analyses indicate that ASTM D86 may lack the needed precision.

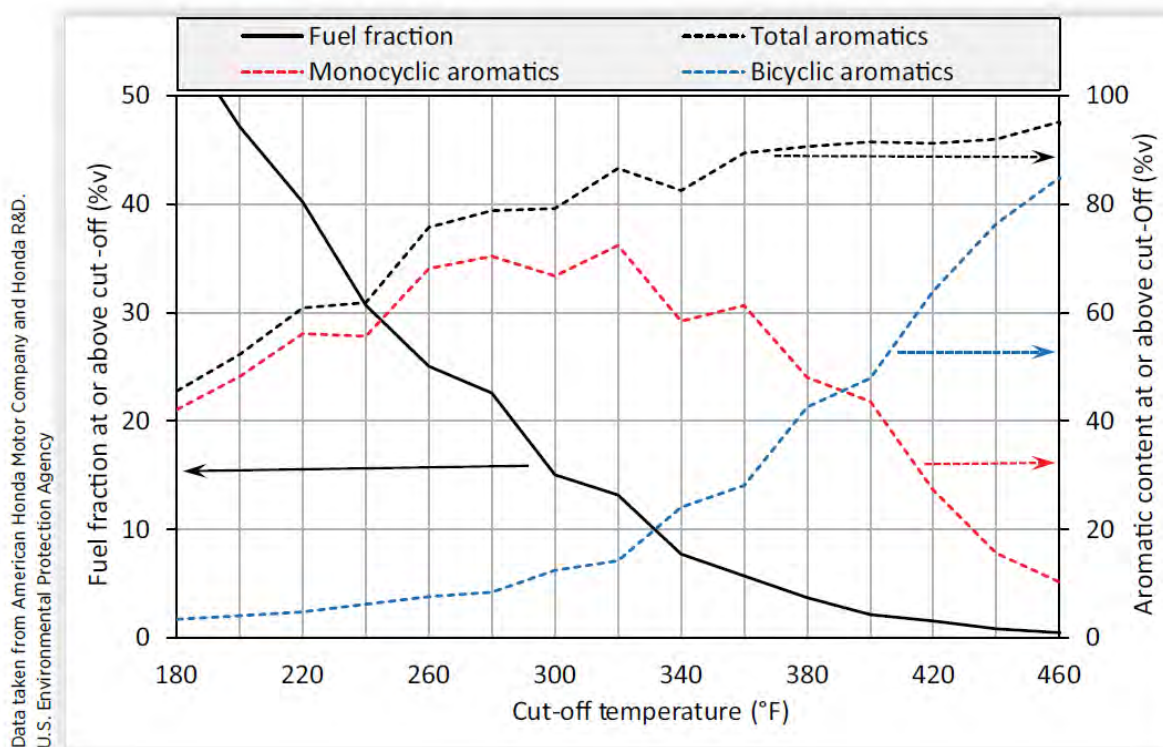
There are a few alternative ASTM chromatography methods that are simpler and faster to run than DHA, which may be better candidates for quantifying heavy aromatics. ASTM D8071 uses a chromatographic column with a vacuum-UV (VUV) spectroscopic detector to produce results by molecular type and carbon number in about 35 minutes. It doesn't quantify individual species but produces percent by carbon number and molecular type (i.e., aromatics, paraffins, naphthenes) that agree well with DHA without requiring the level of operator effort and

expertise as DHA. However, it is a relatively new and unfamiliar method to many labs. Another method is D5769, which quantifies a range of aromatics species using a mass spectrometer but does not offer a complete accounting of all aromatic material.

Simulated distillation (SimDis) by D7096 is a promising option. Unlike D6730 or D8071, this method does not separate the constituents by molecular type but produces a profile of volume (or mass) by boiling point that can be sufficiently precise to quantify the heavy tail of a fuel sample. SimDis was developed in the 1980s to quickly assess the boiling point range of petroleum samples and has been in use in refinery process control for many years. In a lab setting, D7096 runs in about 15 minutes and can easily be incorporated into an automated workflow. Given the data showing that the heavy tail of market gasoline is highly aromatic, this method can act as a promising surrogate for PM-forming compounds.

Figure 2.1 illustrates the highly aromatic nature of the tail of US gasoline based on DHA data from 708 summer regular-grade E10 gasoline market samples [12]. To characterize the distribution of aromatic species, these data were grouped into three categories: total aromatics, monocyclic aromatics (substituted benzenes), and bicyclic aromatics such as naphthalenes. Their percent content in the tail end of the fuels is presented as a function of boiling temperature, with lines indicating the fraction of material boiling above the “cut-off temperature” on the x-axis.

Figure 2.1 also shows the volume fraction of all identified species in the 708 fuels boiling at or above the cut-off temperature. This analysis illustrates that aromatic species dominate the heavy end of US market gasolines, exceeding 90 v% at a cut-off temperature of 380°F. Bicyclic aromatics, which are most prone to the generation of PM emissions, dominate its heaviest, least volatile fractions. It is important to note that these heaviest fractions also contain a significant amount of unidentified species, which are not accounted for in a DHA-based PM Index determination. A SimDis-based approach does not have this problem, given that all component peaks (above a certain noise threshold) are included in the integration with no identification required.



**Figure 2.1. The content of aromatic species in the tail ends of US summer E10 regular-grade market gasoline. [12]**

### **Correlating Fuel Properties with PM Emissions – The Traditional PM Index Approach**

The PM Index is currently the parameter most frequently used to characterize the propensity of gasoline to generate PM emissions. It was proposed in 2010 by Aikawa and colleagues [3]. The PM Index requires the use of a detailed hydrocarbon analysis (DHA) of the fuel and is calculated using the following equation:

$$\text{PM Index} = \sum_{i=1}^n \left[ \frac{(\text{DBE}_i + 1)}{\text{VP}(443\text{K})_i} \times \text{Wt}_i \right]$$

where  $\text{DBE}_i$  is the double bond equivalent of compound  $i$ ,  $\text{VP}(443\text{K})_i$  is the vapor pressure of compound  $i$  at 443 K, and  $\text{Wt}_i$  is the weight percent of compound  $i$  in the fuel.

$\text{DBE}_i$  is related to the degree of saturation of each compound, and therefore to its sooting tendency while the VP term is related to the volatility of each component. In this way the chemical and physical attributes, respectively, of each compound are considered. Heavy aromatic compounds—such as naphthalenes—are highly unsaturated and have low vapor pressures. Considering the equation above, it is clear why such fuel components are main contributors to the PM Index values of commercial gasolines.

However, the complexity and time burden of the required DHA make the PM Index determination more suitable for a research laboratory environment. It would be impractical for routine use in many industrial settings, such as a refinery laboratory.

## **Correlating Fuel Properties with PM Emissions – The SimDis Approach**

The efficacy of the SimDis cut-point (also called endpoint or final boiling point) concept was simulated using the aforementioned DHA database of 708 fuels. Since both SimDis and DHA methods use a GC-FID system to separate a sample by volatility, this exercise provides useful insight. An analysis was undertaken to assess the impact of a range of SimDis cut-points on the average PM Index of US summer, regular-grade E10 gasoline [12]. This activity involved the following steps:

1. Unidentified species were accounted for in the DHA data, and the calculated PM Index was adjusted accordingly for each fuel. This involved the estimation of boiling points, vapor pressures at 443K, and DBEs for the unidentified compounds.
2. Various SimDis cut-points were applied to the 708 gasoline datasets. This involved mathematical trimming of the material boiling at and above the assumed cut-off temperature.
3. To compensate for octane loss, the mass percentage contents of all monocyclic aromatic species boiling below the cut-point were proportionally increased to equal the total mass of heavy material trimmed from each fuel. This procedure also compensated for the loss of mass.

The results of this analysis<sup>1</sup> are shown in Figure 2.2. As this figure demonstrates, a simulation of relatively modest SimDis trims produced significant reductions in the average PM Index of US summer, regular-grade E10 gasoline. For example, a 25% drop in the PM Index from 1.95 to 1.46 could be achieved with a volume trim of about 1%.

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<sup>1</sup> Figure 2.2 represents supplemental results from methods described in reference 12. Original data source: 2008-2012 US market fuel DHA results provided by Honda R&D Americas, Inc.



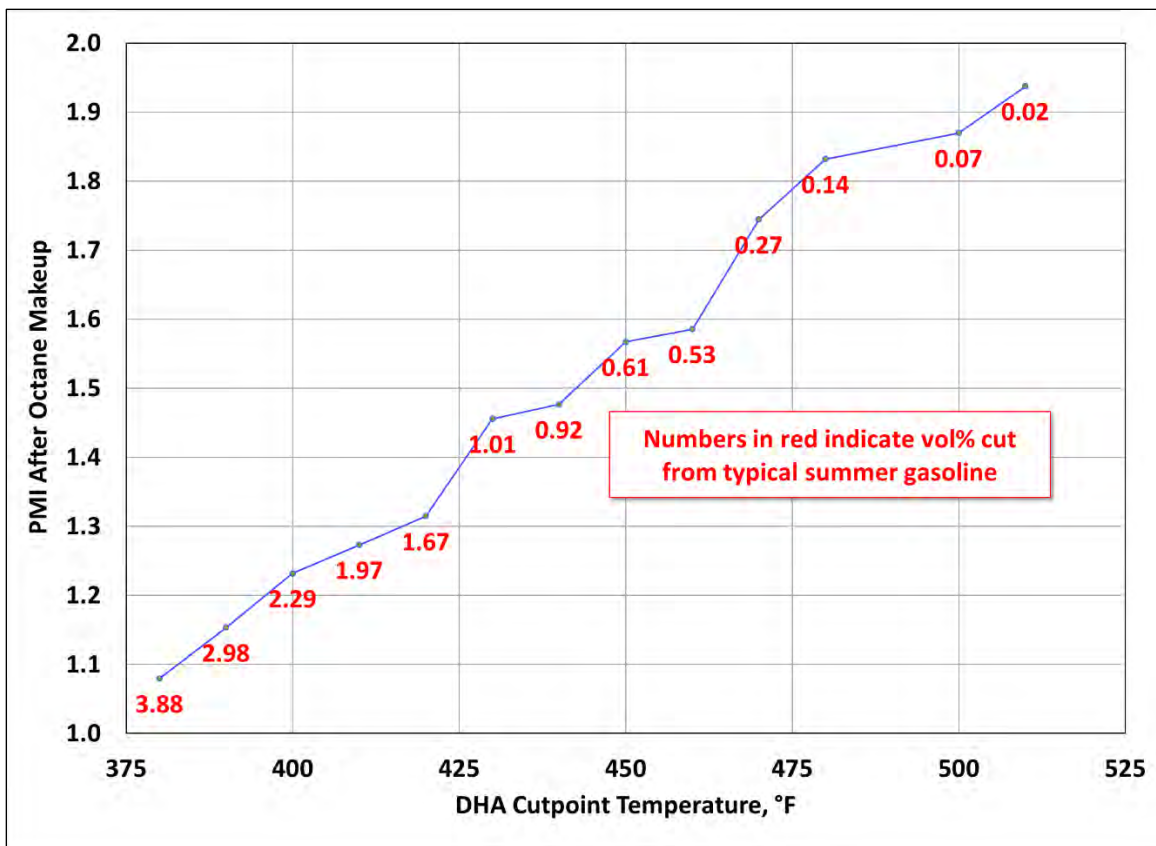


Figure 2.2. Estimated average PM Index of US summer, regular-grade E10 gasoline after SimDis trim and octane makeup as a function of tail cutpoint temperature.

### 2.3. SimDis Investigation Overview

A research program was conducted by several auto manufacturers, a private laboratory, and the US EPA. The program was designed to confirm several assumptions of the SimDis analytical approach. These assumptions are listed in Table 2.1 along with associated project activity. The remainder of this paper will present the SimDis methodology program activities in detail.

**Table 2.1. Objectives of the SimDis methodology investigation program.**

<b>Assumption</b>	<b>SimDis Program Activity to Confirm</b>
<ul style="list-style-type: none"> <li>• The SimDis method can be sufficiently precise to allow reproducible inter- and intra-laboratory determination of the resulting distillation curve, especially in the heavy tail region of the fuel.</li> </ul>	<ul style="list-style-type: none"> <li>• Enhance ASTM D7096 interlaboratory precision through improvements to procedures, sample handling and instrument parameters while staying within the bounds of the ASTM method itself.</li> <li>• Perform an interlaboratory study to confirm the resulting improvement in precision.</li> </ul>
<ul style="list-style-type: none"> <li>• SimDis data parameters correlate with DHA-based PM Index data, thereby confirming analysis by SimDis to be a compelling alternative method for assessing the PM-formation propensity of a fuel.</li> </ul>	<ul style="list-style-type: none"> <li>• Acquire multiple market fuels and perform DHA and SimDis analyses.</li> <li>• Analyze the correlation between the PM Index of the fuels and various parameters derived from resulting SimDis data.</li> </ul>

### 3. Simulated Distillation (SimDis) Methodology Improvements

#### 3.1. Overview of ASTM D7096

Several simulated distillation methods have been developed and standardized by ASTM. Simulated distillation is used to determine the boiling point distribution of crude oil and petroleum refining fractions through the use of gas chromatography (GC). Typically, hydrocarbon samples are eluted from a nonpolar column in boiling-point order by temperature programming until the entire sample is eluted. For gasoline simulated distillation several standardized procedures exist, including ASTM D7096. This method provides a rapid determination of a gasoline's chemical profile based on boiling point ranges using a large-bore, non-polar separation column. The SimDis methodology is analogous to physical distillation, which is more time consuming and doesn't provide fine resolution in the boiling point distribution due to low (single plate simulation) efficiency. A typical gasoline fuel sample may contain up to 1000+ compounds, with many of them being isomers with azeotropic boiling behavior. This makes deeper analysis of low-efficiency distillation (e.g., ASTM D86) data difficult. Analysis by GC typically has better precision, higher throughput, less hands-on time, and lower cost per sample. SimDis also requires considerably less sample for analysis; less than 1 ml as compared to D86 which requires a minimum of 100 ml.

ASTM D7096 is among the newest SimDis methods for gasoline. The combination of large-bore, thick film columns and flame ionization detection yields a robust, reproducible analysis. Extracting distillation curves from GC data starts by slicing a chromatogram into very small segments and integrating the area under the signal. Boiling points for each slice are interpolated from reference standards eluting before and after the slice. The cumulative sum of volumes of individual slices are plotted against the boiling points of those slices to yield a boiling point curve.

#### 3.2. Lab Work to Enhance ASTM D7096

Despite the advantages of simulated distillation by GC, the method has not been widely adopted by analytical laboratories. Part of this is due to the fact that most fuel specifications require distillation data be obtained through ASTM D86, which is the more traditional method. However, with advancements in both hardware, software, and methodology, SimDis can provide more precise and detailed information for a given sample. In an effort to evaluate and improve the usefulness of this method, work was performed to further specify ASTM D7096 analytical conditions, sample, and data handling to improve both inter and intra-laboratory precision while also remaining within the bounds of the ASTM method itself.

This work was done in three stages between the GM Pontiac and US EPA NVFEL laboratories followed by sample exchanges with other labs running the D7096 method with proposed enhancements to validate improvements to the method.

##### 3.2.1 Stage One – Initial Investigation

Stage One was composed of an initial investigation into method reproducibility using the currently in-use methods at the GM Pontiac and US EPA laboratories. Five samples were exchanged, and each lab analyzed the samples using the method their lab currently uses for ASTM D7096 analysis, generating distillation curves. As this project focuses on heavy gasoline components, results below the 50% distilled mark were calculated but are not presented. Resulting absolute differences for each of the six Stage One samples can be seen in Table 3.1 alongside the ASTM D7096 method precision (ASTM R).

**Table 3.1. Absolute Differences Exchange Samples Compared with ASTM Reproducibility (°F).**

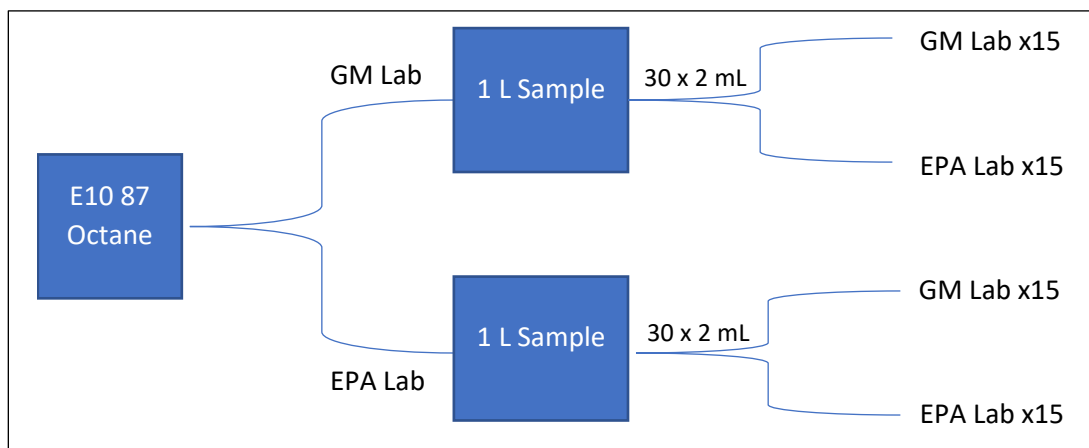
T-number (%-off)	ASTM R	Fuel S1-1	Fuel S1-2	Fuel S1-3	Fuel S1-4	Fuel S1-5	Fuel S1-6
50	17.8	0.8	7.2	3.1	2.8	3.4	1
70	18	11.8	8.6	0.1	1.9	5	5.5
80	3.2	19.3	1.4	9.3	7.7	8.6	37.9
90	6.7	11.1	0.9	3.3	10.3	16.4	7
95	8.3	16	2.4	3.6	14.2	17.1	3.5
FBP	18.5	15	4.1	57.9	54.2	39.8	15.9

While some data points show good alignment to the documented ASTM D7096 reproducibility, a large majority of the data above T80% falls outside the current method precision. Since the focus of this work is on the heavy end components, the source of this variation should be reduced. Various elements of the method were investigated to find and reduce the variation as much as possible.

The first step was to review each lab’s procedures on paper to determine any areas of difference. Differences found included sample handling, analytical sample sequence order, hold time at the end of a run (260°C), injection blanks used for baseline subtraction, and whether a lab was using a pre-sequence column bake or not. All of these differences, though seemingly incidental, can result in analytical variances. As a result, both labs deemed it necessary to conduct further investigation through a variety of studies aimed at choosing the most reliable methodology to obtain more precision.

### 3.2.2 Stage Two – Method Refinement

In Stage Two, a second sample exchange was conducted with the goal of isolating sources of variation and eliminating them. A sample preparation procedure was agreed upon, wherein samples would be shipped same-day on ice, refrigerated on arrival, aliquoted cold into 2 mL GC vials and sealed with crimp caps and analyzed within a week of receipt. The sample exchange included a single gasoline source, shipped in a 1 L bottle to each lab. The lab then aliquoted the sample into thirty 2 mL vials and shipped half to each other. In this way, any sample preparation variations could be deduced if present. A diagram demonstrating sample prep can be seen below in Figure 3.1.



**Figure 3.1. Sample Exchange #2 sampling diagram.**

Results of the sample exchange can be seen below in Table 3.2. Samples prepared by the GM lab are shown on the left while samples prepared by the EPA lab are shown on the right. Notice that although the results when compared between labs show a large absolute difference, when comparing data within the same lab, the repeatability is very good regardless of which lab prepared the samples. This indicates there is a method difference causing the variability and not a sample handling issue.

**Table 3.2. Stage Two Sample Exchange Results. Green boxes denote results within ASTM R, yellow boxes denote within 1°F of R and red boxes denote results outside the R.**

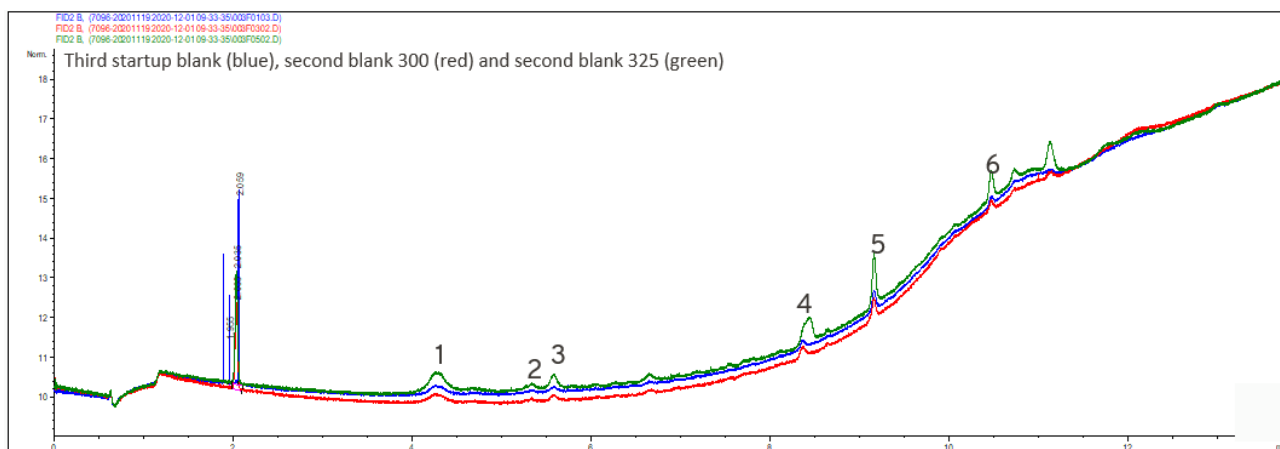
	Sample Prep by GM			Sample Prep by EPA		
	GM Analyzed Average value (°F)	EPA Analyzed Average value (°F)	Difference	GM Analyzed Average value (°F)	EPA Analyzed Average value (°F)	Difference
IBP	46.5	28.2	18.3	46.3	27.6	18.7
5	54.7	50.3	4.4	54.5	49.7	4.8
15	78.6	64.7	13.9	72.6	55.2	17.4
25	83.6	88.7	5.2	83.3	84.9	1.6
35	97.6	120.2	22.7	97.3	106.0	8.7
45	139.7	154.2	14.5	139.0	150.4	11.4
55	157.9	190.8	33	156.7	186.7	30
65	196.8	213.1	16.3	195.0	209.3	14.3
75	230.9	249.1	18.2	230.3	242.3	11.9
85	282.6	299.2	16.6	281.1	293.7	12.6
90	335.2	341.9	6.7	327.8	341.3	13.5
95	384.6	387.9	3.3	376.2	383.9	7.7
FBP	496.1	474.8	21.3	491.6	474.3	17.4

### 3.2.3 Stage Three – Further Refinement, Harmonized Method

Going into Stage Three, the following parameters were examined through a series of studies: injection volume, inlet temperature, and final temperature hold time. The studies and their results are paraphrased below.

#### A. Inlet Temp Study

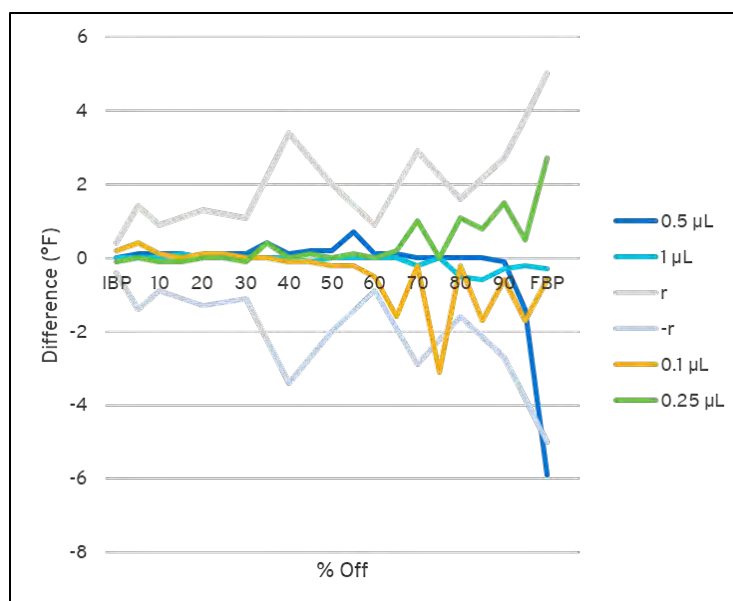
- Objective: Determine whether raising inlet temperature to 325°C reduces carryover between runs.
- How: Inject 0.5  $\mu\text{L}$  standard followed by two method blank injections (no physical injection) at 300°C and 325°C.
- What to measure: Compare first blanks with one another and with second blanks.
- Expected Outcome: Determine most consistently clean blank.
- Result: 325°C increased septum bleed peaks and carryover (Figure 3.2). Use 300°C for inlet temperature.



**Figure 3.2. Method blank chromatogram overlay showing the startup blank (blue trace), second blank with inlet at 300°C (red trace) and second blank with inlet at 325°C (green trace). Larger peaks at a higher inlet temperature imply more septum bleed is occurring.**

#### B. Injection Volume Study

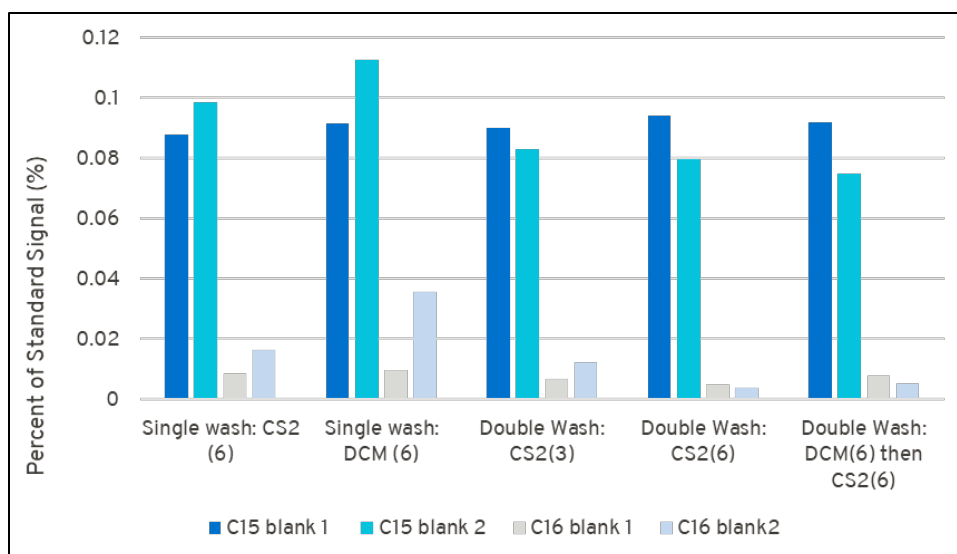
- Objective: Determine the effect of injection volume on carryover and initial boiling point (IBP).
- How: Use 3X air injection blanks, then inject 0.1, 0.25, 0.5 and 1  $\mu\text{L}$  of standard followed by two more air injection blanks. Inject reference fuel at each level. Use 0.5  $\mu\text{L}$  syringe for 0.1 and 0.25  $\mu\text{L}$ . Use 5  $\mu\text{L}$  syringe for 0.5 and 1  $\mu\text{L}$ .
- What to measure: determine IBP and final boiling point (FBP) for each fuel sample, measure peak area of standard and in blank immediately following standard.
- Expected Outcome: Determine if lower volume decreases ratio of carryover. Determine effect on IBP and FBP.
- Result: Lower injection volumes increase relative carryover and r (Figure 3.3). Use a 1  $\mu\text{L}$  injection.



**Figure 3.3. Absolute difference in reference fuel at different injection volumes with  $\pm$  ASTM r for reference. 1  $\mu$ L injections showed the least variability.**

### C. Syringe wash study

- Objective: Determine the effect of different syringe wash programs on carryover using carbon disulfide ( $\text{CS}_2$ ) and dichloromethane (DCM) wash solvents.
- How: 3X method blanks, THEN Inject 0.5  $\mu$ L standard followed by two more method blank injections for: wash vial A only ( $\text{CS}_2$  and DCM), wash vials A&B ( $\text{CS}_2$ , 3 and 6 washes) and vial A ( $\text{CS}_2$ ) then vial B (DCM) washes. Inject samples from wash bottles to determine transfer.
- What to measure: Measure the peak area of  $\text{C}_{15}$  and  $\text{C}_{16}$  in the sample and in the blank immediately following the standard, inspect 1st blank vs. 2nd blank.
- Outcome: Determine conditions that minimize carryover.
- Results: A dual solvent system with DCM followed by  $\text{CS}_2$  using 6 solvent rinses performed best, though all double-wash procedures performed better than single wash (Figure 3.4).



**Figure 3.4. Results of the syringe wash study. A dual wash system generally works best and 6 washes in each vial works better than only 3 washes.**

#### D. Blank Study

- Objective: Determine whether to use solvent blank, method blank, or air blank between sample injections.
- How: 3X method blanks, then inject 0.5  $\mu\text{L}$  standard followed by two more method blank injections of a) air, b) nothing and c)  $\text{CS}_2$ .
- What to measure: Compare first blanks with one another and with second blanks.
- Outcome: Determine most consistent blank.
- Caveat: Operator noticed an issue with the air blanks wherein standard compound carryover was evident and greater with the second blank, suggesting syringe carryover into air-blank vial caused contamination.
- Results: DCM solvent peak dominates and doesn't seem to provide any improvements over  $\text{CS}_2$ . Two  $\text{CS}_2$  blanks provide least amount of sample-to-sample carryover.

After collating and implementing learnings from the studies conducted in Stages One and Two above, a final method was decided upon. This method was written up as a standard operating procedure covering GC method parameters, blank selections, and sample handling and storage requirements. See Appendix A for the procedure distributed to laboratories participating in sample exchanges.

Summary of proposed final method and sample procedure:

- Oven: 40°C 1 min, 25 °C/min to 260 °C, 4 min hold, 6 min post run @40 °C
- Injection Volume: 1  $\mu\text{L}$
- Wash 6X DCM (or  $\text{CS}_2$ ), 6X  $\text{CS}_2$
- Injection: 300°C, Split 50:1, Focus liner w/glass wool
- Carrier Gas: He, 5 mL/min for 0.6 min, 30 mL/min<sup>2</sup> to 20 mL/min
- Detector: FID, 300°C, 30 ml/min combined makeup
- Batch sequence order controlled
- Run 3 method blanks before sample injections and use third blank for baseline subtraction



- Two CS<sub>2</sub> blanks run between each sample
- Calibration performed with each batch of samples
- Use crimp cap vials and ensure proper sealing before analysis
- Store and aliquot samples cold (0 - 4°C when transferring liquid)

### 3.3. Sample Exchange Validation

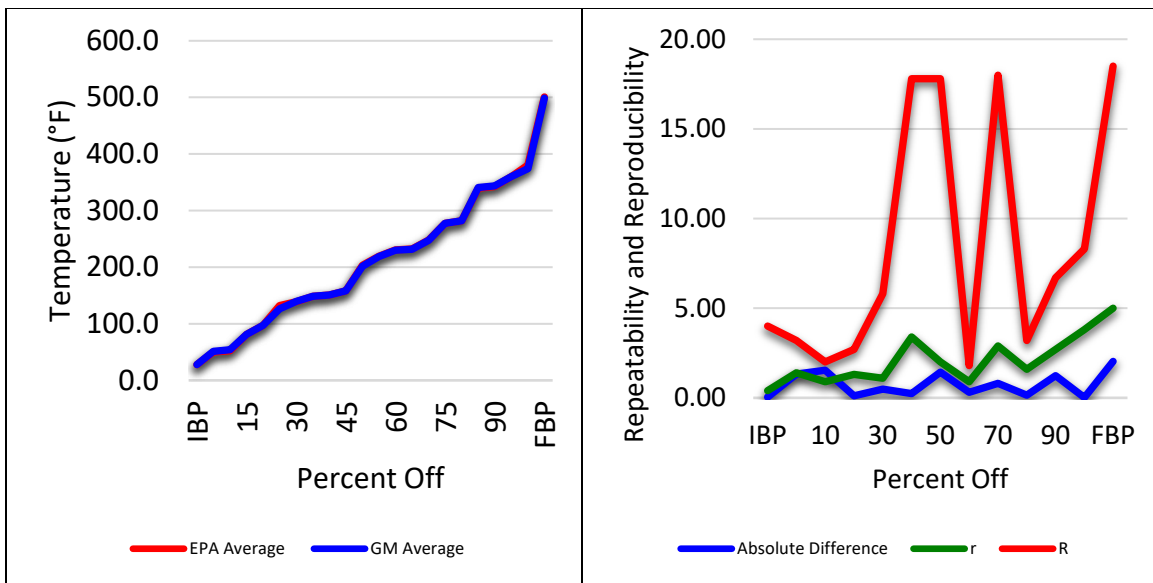
#### 3.3.1 Sample Exchange Validation

A sample exchange study was performed between the GM Pontiac Chemistry Laboratory and the EPA lab, incorporating what was learned in previous steps. The results are presented in Table 3.3 and Figure 3.5 and show:

- Both labs improved repeatability over previous stages
- Average results from EPA and GM within *repeatability* (*r*) of one another at 12/13 points
  - < 2 °F difference
  - Within *reproducibility* (R) at 13/13 points
- Deviation at 2 points with no calculated statistics
  - T25 and T98
    - T25 GM found 2 replicates at 122 °F and 1 at 134 °F
    - T25 EPA found 1 replicate at 122 °F and 5 at 134 °F

**Table 3.3. Distillation data from the same fuel performed at both EPA and GM Laboratories.**

	EPA Average °F	GM Average °F	Abs. Dif. °F
IBP	27.80	27.83	0.03
5	50.10	51.43	1.33
10	52.50	54.03	1.53
15	81.05	81.00	0.05
20	96.95	97.07	0.12
25	132.25	126.23	6.02
30	139.02	139.50	0.48
35	148.53	148.47	0.07
40	150.60	150.83	0.23
45	158.18	158.07	0.12
50	203.30	201.87	1.43
55	219.17	218.87	0.30
60	230.38	230.07	0.32
65	232.05	231.87	0.18
70	248.07	247.27	0.80
75	277.38	277.33	0.05
80	282.08	282.23	0.15
85	339.67	340.50	0.83
90	342.47	343.70	1.23
95	360.12	360.13	0.02
98	380.38	374.37	6.02
FBP	500.77	498.73	2.03



**Figure 3.5. EPA and GM SimDis profile overlay and ASTM r & R values compared to absolute differences between labs, plotted at 10-degree intervals.**

### 3.3.2 Sample Exchange Study on Five Test Fuels

The five fuels used in the emissions study (Table 3.4) were analyzed by the enhanced ASTM D7096 SimDis method at both the GM Pontiac chemistry lab and Southwest Research Institute (SwRI) in San Antonio, Texas. The fuel samples were blinded to avoid any operator bias. Two operators in Pontiac lab performed the analysis on the same GC, while SwRI used one operator. As a comparison, the conventional distillations by D86 are also listed in the Table 3.5 along with SimDis D7096. The distillation by D86 were performed by three labs: GM Pontiac Chem Lab, EPA NVFEL, and Gage Products in Ferndale, Michigan.

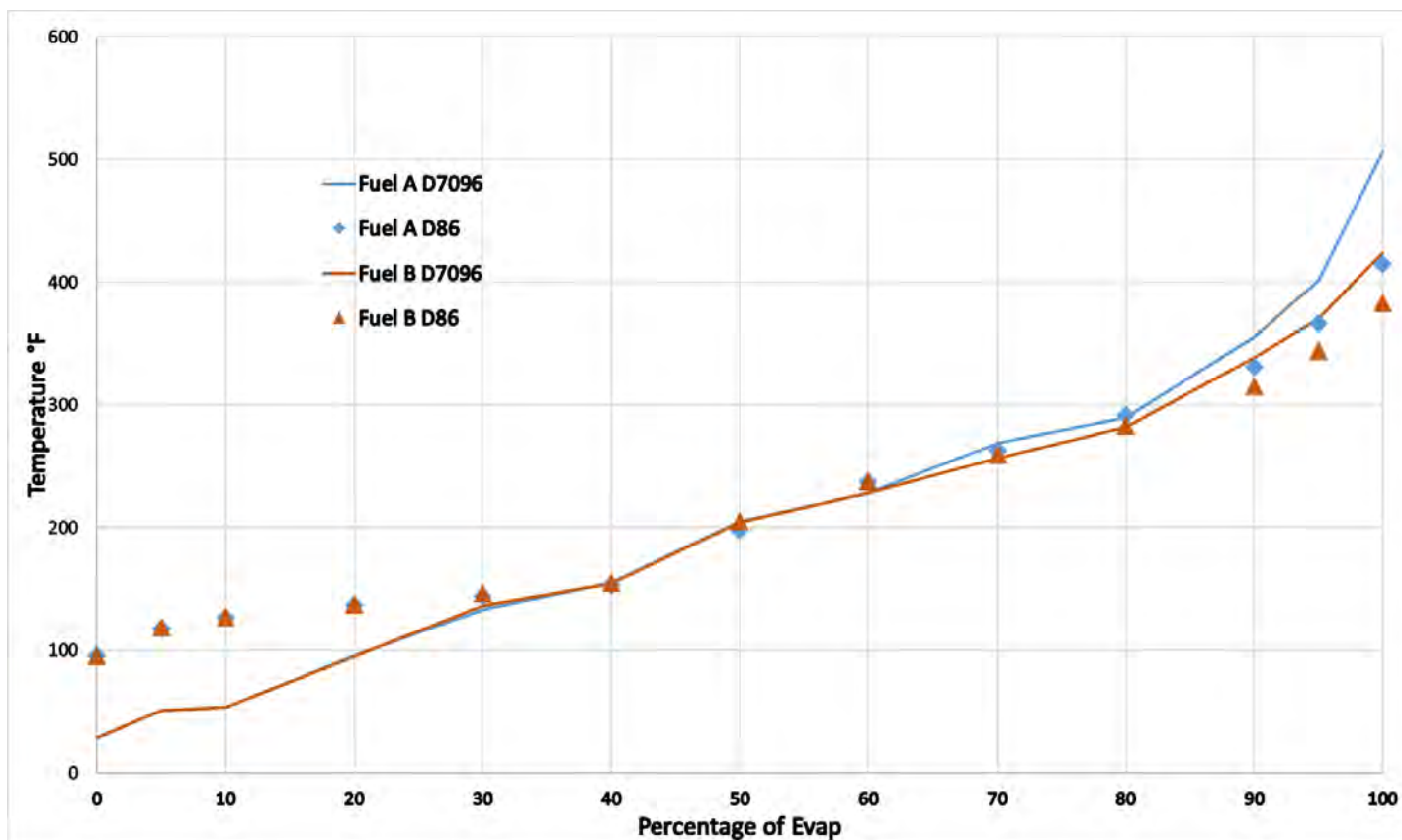
**Table 3.4. Final fuel property data after blending.**

Parameter	Unit	Method	Blending Tolerance	Base Fuel (Typical regular-grade gasoline)		Fuel A (Base Fuel w/3.1 vol.% of C10+ Aromatics)		Fuel B (Base Fuel w/3.1 vol.% of C7-C9)		Fuel C (Base Fuel w/3.1 vol.% of alkylate)		Fuel D (Base Fuel w/6 vol.% of ethanol)			
				Specification	Average	Specification	Average	Specification	Average	Specification	Average	Specification	Average		
Density @ 60°F	g/cm <sup>3</sup>	D4052	-	-	0.7428	-	0.7490	-	0.7477	-	0.7420	-	0.7457		
Specific Gravity @ 60°F	-	D4052	-	-	0.7435	-	0.7497	-	0.7484	-	0.7428	-	0.7465		
PMI Index by Gage DHA	-	Gage DHA	± 0.1	1.5	1.49	2.66	2.72	1.58	1.53	1.46	1.50	1.42	1.41		
Ethanol	vol. %	D4815	± 0.2	10	9.54	9.7	9.27	9.7	9.24	9.7	9.23	14.9	14.75		
Other Oxygenates	vol. %		maximum	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.1	0.0		
Oxygen	mass %	-	-	-	3.54	-	3.43	-	3.43	-	3.42	-	5.48		
RON	-	D2699	-	-	91.1	-	91.4	-	91.7	-	91.2	-	93.8		
MON	-	D2700	-	-	83.2	-	83.5	-	83.7	-	83.7	-	84.6		
(R + M)/2	-	D2699/D2700	± 0.3	87.2	87.2	87.4	87.5	87.5	87.6	87.2	87.4	89.2	89.2		
Sensitivity	-		-	-	7.9	-	7.9	-	7.9	-	7.5	-	9.2		
DVPE	psi	D5191 (EPA)	± 0.2	9.0	9.2	8.6	9.1	8.7	8.9	8.7	9.0	8.7	9.1		
Distillation															
IBP		°F	D86	-	-	95.1	-	95.6	-	96.1	-	95.5	-	96.0	
T5				-	-	117.0	-	118.7	-	118.9	-	118.3	-	119.4	
T10				± 5	127.6	125.0	128.6	126.5	128.9	127.2	128.1	126.2	129.3	127.2	
T20				-	-	135.6	-	137.2	-	137.7	-	136.6	-	137.9	
T30				± 5	146.1	144.9	147.3	146.4	147.5	146.9	146.5	145.8	148.3	147.2	
T40				-	-	152.6	-	154.7	-	155.6	-	153.5	-	155.0	
T50				± 5	196.7	192.9	207.2	205.1	206.3	204.8	202.1	199.8	161.7	161.5	
T60				-	-	232.8	-	240.0	-	237.7	-	232.8	-	218.9	
T70				± 5	256.8	255.5	264.3	264.6	260.0	259.7	255.1	255.7	253.6	252.9	
T80				-	-	280.7	-	292.8	-	283.2	-	279.9	-	278.6	
T90				± 5	313.9	312.0	331.5	331.9	313.3	315.6	314.1	312.0	311.6	311.3	
T95				-	-	344.1	-	367.9	-	345.4	-	344.4	-	342.3	
FBP				-	-	maximum	437	380.1	437	420.3	437	382.0	437	383.2	437
Residue, vol. %				-	-	maximum	1.3	1.0	1.3	1.1	1.3	1.0	1.3	1.0	1.3
Recovery	%v			-	-	-	97.4	-	97.9	-	97.8	-	98.1	-	98.1
Loss		-	-	-	1.5	-	1.5	-	1.6	-	1.5	-	1.5		
Total Aromatics		%v	(Gage DHA)	± 1	25.0	24.6	27.3	26.8	27.5	27.3	24.2	24.1	23.6	23.2	
Benzene				± 0.2	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	
Toluene				± 1	6.3	6.2	6.1	6.0	7.1	7.3	6.1	6.0	7.9	5.9	
C8 Aromatics				± 1	8.1	8.1	7.9	7.8	9.0	8.9	7.8	7.9	5.9	7.6	
C9 Aromatics				± 1	5.5	5.3	5.4	5.2	6.3	6.0	5.4	5.2	5.2	5.0	
C10 Aromatics				± 1	3.4	3.3	4.9	4.7	3.5	3.3	3.3	3.2	3.2	3.0	
C11+ Aromatics		± 0.3	1.1	1.2	2.4	2.5	1.1	1.2	1.1	1.2	1.0	1.2			
PM Index by D6729	-	-	-	-	1.43	-	2.28	-	1.46	-	1.44	-	1.37		
Total Aromatics		%v	D6729	-	-	25.1	-	27.7	-	27.3	-	24.8	-	24.1	
Benzene				-	-	0.6	-	0.6	-	0.6	-	0.6	-	0.6	
Toluene				-	-	6.7	-	6.5	-	7.8	-	6.3	-	6.4	
C8 Aromatics				-	-	7.9	-	7.7	-	8.6	-	7.8	-	7.5	
C9 Aromatics				-	-	5.4	-	5.4	-	6.0	-	5.4	-	5.2	
C10 Aromatics				-	-	3.0	-	4.5	-	3.0	-	3.1	-	2.9	
C11+ Aromatics		-	-	1.6	-	3.0	-	1.4	-	1.6	-	1.4			
PM Index by D6730-1X	-	-	-	-	1.48	-	0.00	-	1.53	-	1.45	-	1.41		
Total Aromatics		%v	D6730-1X	-	-	24.7	-	0.0	-	27.4	-	24.0	-	23.4	
Benzene				-	-	0.6	-	0.0	-	0.6	-	0.6	-	0.6	
Toluene				-	-	6.3	-	0.0	-	7.4	-	6.1	-	5.9	
C8 Aromatics				-	-	7.9	-	0.0	-	8.8	-	7.7	-	7.6	
C9 Aromatics				-	-	5.3	-	0.0	-	6.0	-	5.2	-	5.1	
C10 Aromatics				-	-	3.0	-	0.0	-	3.0	-	2.9	-	2.8	
C11+ Aromatics		-	-	1.5	-	0.0	-	1.5	-	1.5	-	1.5			
Olefins	%m	D6550	± 3	7	8.7	7	8.5	7	8.7	7	8.4	7	8.1		
Sulfur	mg/kg	D5453	± 3	7	6.3	7	6.0	7	6.0	7	6.1	7	5.8		
Carbon (Part of D4809)	mass %	D5291	-	-	82.62	-	82.98	-	82.99	-	82.82	-	80.86		
Hydrogen (Part of D4809)	mass %	D5291	-	-	13.72	-	13.49	-	13.44	-	13.70	-	13.61		
Carbon	mass %	D3343M	-	-	82.70	-	82.98	-	82.96	-	82.71	-	80.99		
Hydrogen	mass %	D3343M	-	-	13.64	-	13.5	-	13.47	-	13.81	-	13.49		
Water Content	mg/kg	E1064	-	-	1315	-	1259	-	1256	-	1314	-	1925		
Lead	g/l	D3237	-	≤ 0.013 g/l	< 0.0027	≤ 0.013 g/l	< 0.0027	≤ 0.013 g/l	< 0.0027	≤ 0.013 g/l	< 0.0027	≤ 0.013 g/l	< 0.0027		
Net Heat of Combustion (D240)	MJ/kg	D240	-	-	41.58	-	41.63	-	41.56	-	41.78	-	40.74		
Net Heat of Combustion-D1319	MJ/kg	D3338	-	-	41.36	-	41.34	-	41.31	-	41.79	-	40.40		
Oxidation Stability	minute	D525	minimum	240	> 1,000	240	> 1000	240	> 1000	240	> 1000	240	> 1000		
Copper Strip Corrosion, 3h at 122°F	-	D130	maximum	No. 1	1A	No. 1	1A	No. 1	1A	No. 1	1A	No. 1	1A		
Solvent-Washed Gum Content	mg/100 ml	D381	maximum	5	< 0.5	5	< 0.5	5	< 0.5	5	< 0.5	5	< 0.5		
T <sub>v(L20)</sub>	°F	D5188	minimum	116	128.7	116	129.7	116	130.3	116	129.8	116	129.3		
Driveability Index	-	D4814	maximum	1250	1101	1250	1159	1250	1143	1250	1123	1250	1022		

**Table 3.5. Distillation data on five fuels.**

Distillation, °F		Base		Fuel A		Fuel B		Fuel C		Fuel D	
	Method	Std	Avg.	Std	Avg.	Std	Avg.	Std	Avg.	Std	Avg.
0	D7096	0.283	28.4	0.308	28.7	0.367	28.6	0.418	28.5	0.427	28.6
5	D7096	0.827	50.8	0.850	51.1	0.780	51.1	0.965	50.9	0.852	50.8
10	D7096	0.931	53.4	0.840	53.8	0.860	53.7	0.860	53.7	0.351	53.1
20	D7096	0.500	94.6	0.458	95.5	0.441	95.3	0.531	95.0	7.628	85.7
30	D7096	10.487	126.2	8.937	133.2	2.360	136.6	10.315	131.5	12.371	105.4
40	D7096	2.453	152.2	2.745	155.2	2.455	154.7	2.822	153.8	1.302	149.2
50	D7096	3.576	201.1	0.418	204.5	0.374	204.4	0.838	203.5	5.729	196.2
60	D7096	5.540	214.3	4.828	227.8	3.909	228.0	7.874	218.9	3.201	209.2
70	D7096	1.860	251.0	7.624	269.0	7.846	256.7	1.832	250.4	0.750	248.5
80	D7096	0.332	281.2	3.981	289.8	0.550	281.9	0.425	281.1	0.103	280.8
90	D7096	5.451	335.3	5.231	355.4	3.852	338.4	6.114	335.5	2.390	331.2
95	D7096	4.842	373.9	1.740	401.6	5.891	370.2	5.018	373.8	2.179	371.0
100	D7096	2.132	424.2	7.199	506.1	1.673	423.8	1.826	425.2	0.641	423.9
Distillation, °F											
	Method	Std	Avg.	Std	Avg.	Std	Avg.	Std	Avg.	Std	Avg.
0	D86	1.169	95.5	2.114	95.7	1.997	95.4	1.877	95.7	0.453	94.3
5	D86	0.673	117.2	2.144	117.6	0.696	119.2	2.535	119.5	0.297	119.8
10	D86	0.273	124.9	0.666	126.8	0.321	127.3	1.640	126.9	0.467	127.4
20	D86	1.913	136.6	0.831	136.8	0.129	137.7	1.255	137.0	0.693	137.9
30	D86	1.096	144.2	4.154	144.1	0.452	147.0	0.930	146.0	1.004	147.2
40	D86	2.957	150.4	1.896	153.3	0.423	155.2	2.123	154.7	0.764	154.9
50	D86	22.603	179.6	12.687	198.0	0.867	205.5	0.262	199.9	0.566	161.2
60	D86	21.870	220.7	5.613	237.3	1.152	237.8	1.299	234.3	1.442	219.6
70	D86	8.597	250.0	3.179	262.8	0.589	259.9	1.222	256.3	0.764	253.0
80	D86	6.493	276.9	2.706	291.5	0.621	283.1	1.100	280.2	0.509	278.1
90	D86	4.203	308.3	2.794	330.7	0.924	315.1	2.956	311.2	0.099	310.6
95	D86	6.173	340.6	2.291	366.1	1.594	344.5	1.315	343.2	1.541	341.6
100	D86	11.111	375.6	10.013	414.7	0.356	383.0	4.418	381.9	1.358	382.8

In general, the standard deviations from D7096 SimDis analysis on the five fuels from two labs across three operators are much better than from conventional D86. However, it must be noted there are larger than expected deviations in the 20-40% distillation point range using the enhanced D7096 as compared to the current ASTM D7096 precision. Further study is ongoing with the ASTM D7096 team and the method developer on improvements to the calibration strategy and potential software updates to enable a more reproducible method. Even so, SimDis provides much better resolution and compound separation for gasolines when compared with ASTM D86. A graphical comparison of the D86 vs D7096 distillation profiles for two of the test fuels is shown in Figure 3.6 below. Each data point is averaged across all labs that ran each sample.



**Figure 3.6. Fuel A and Fuel B distillation profiles from D7096 and D86**

As SimDis methodology utilizes capillary column technology and ramping oven temperatures to separate individual fuel components based on boiling point, it provides better resolution and fewer azeotropic interferences throughout the entire distillation profile as can be seen in the figures above. The improved resolution is due to samples being injected into a sealed inlet by micro syringe, resulting in all compounds (light or heavy) making it onto the column with minimal loss. By contrast, in the more traditional D86 distillation, resolution is lost at the back end due to isotropic hydrocarbon interactions and at the front end due to unavoidable sample handling compromises. As a result, the beginning and end of the D86 distillation profile are biased towards the average boiling point of the fuel. The better resolution from SimDis provides a much better option for rapidly determining a fuel's volatility characteristics.

## 4. Application of SimDis Cut-Points and PM Index Analysis to US Market Gasolines

With the improved resolution of the heavy tail of gasoline provided by these SimDis procedures, it becomes feasible to correlate specific SimDis parameters with PMI and other emission indices [13, 14]. In this section, we examine the correlation of SimDis results with PM Index for a set of 80 samples taken from a US retail market survey conducted during 2021-22. These samples were analyzed by both DHA (D6730-X1) and SimDis (D7096). The SimDis analyses were carried out in General Motors Pontiac Chem Lab and the DHA analyses were performed at Southwest Research Institute.

### 4.1 SimDis Results

Figure 4.1 shows four example distillation profiles from SimDis with PMI values ranging from 1.01 to 2.55. A key observation is that points between T90 and T98 fall reliably in order of PMI, with the distance between the lines being roughly proportional to the differences in PMI. This is consistent with the heavy tail material being a primary driver of the overall PMI value.

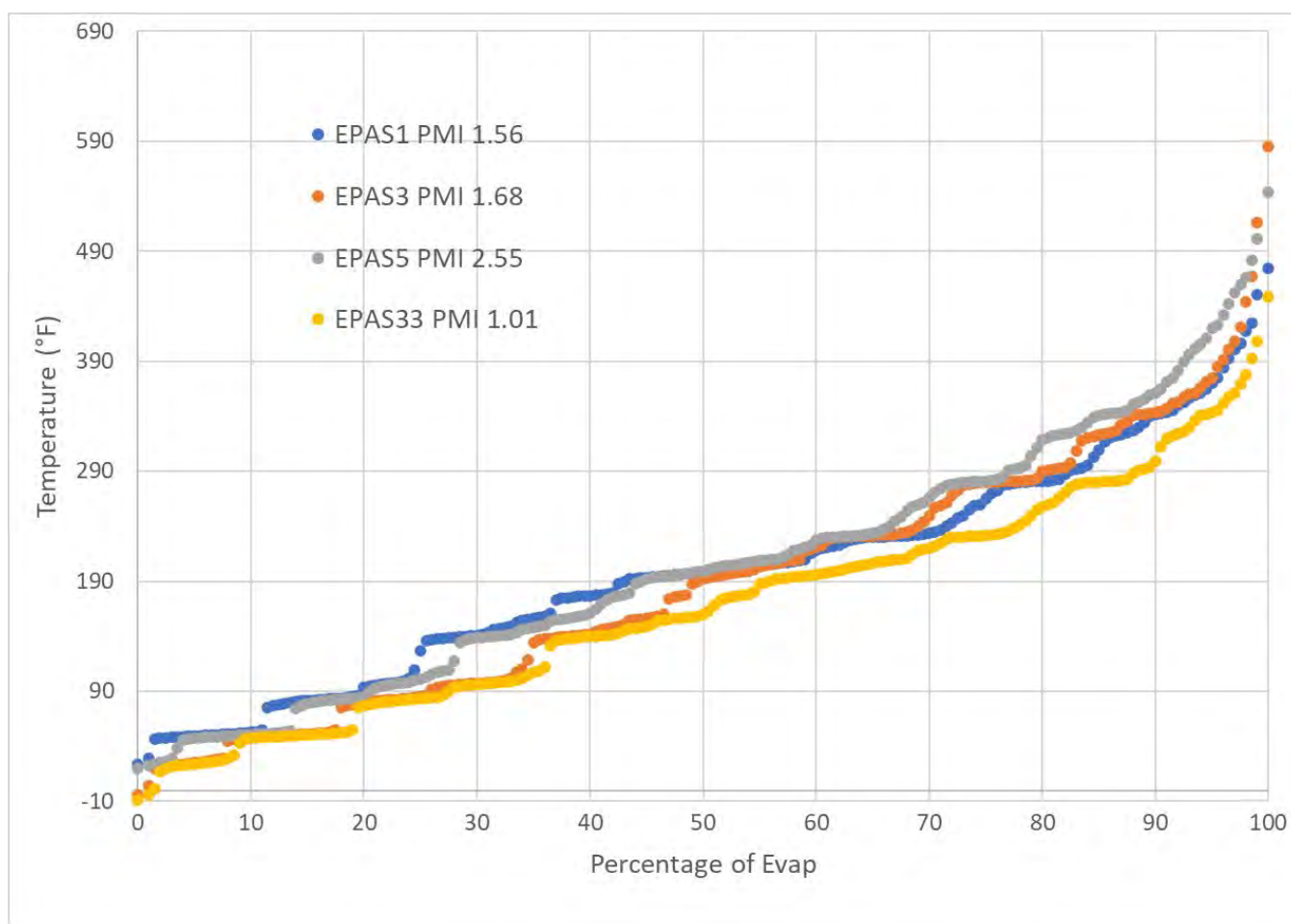
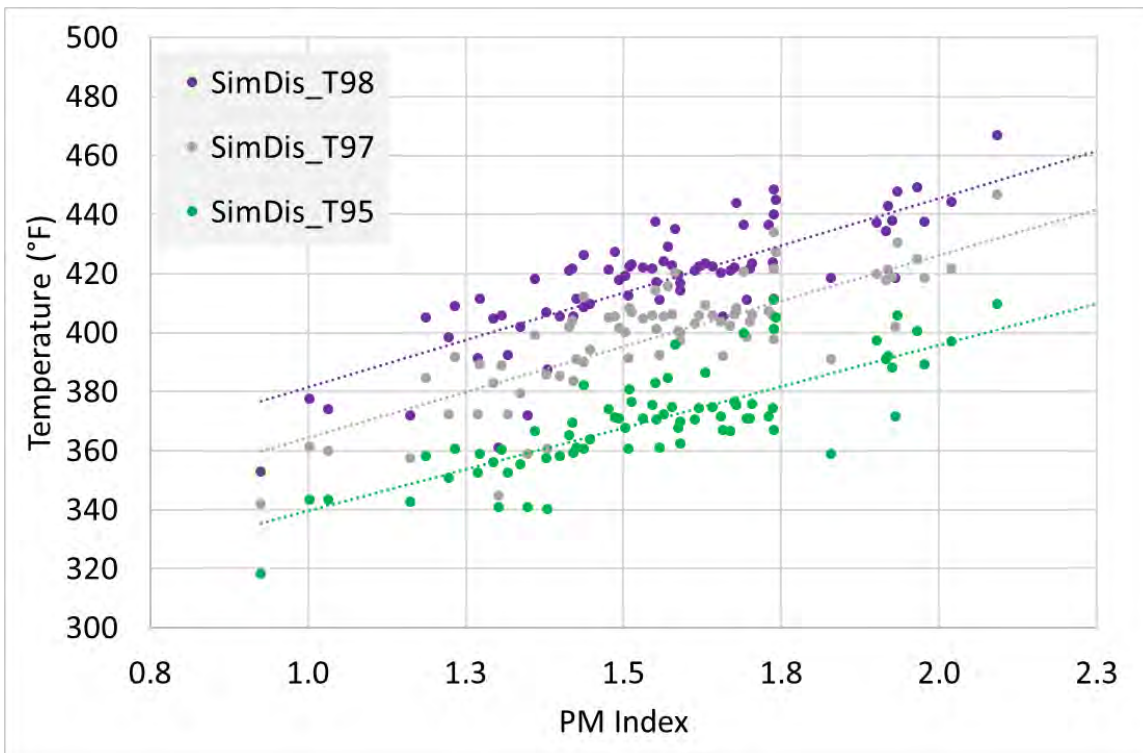
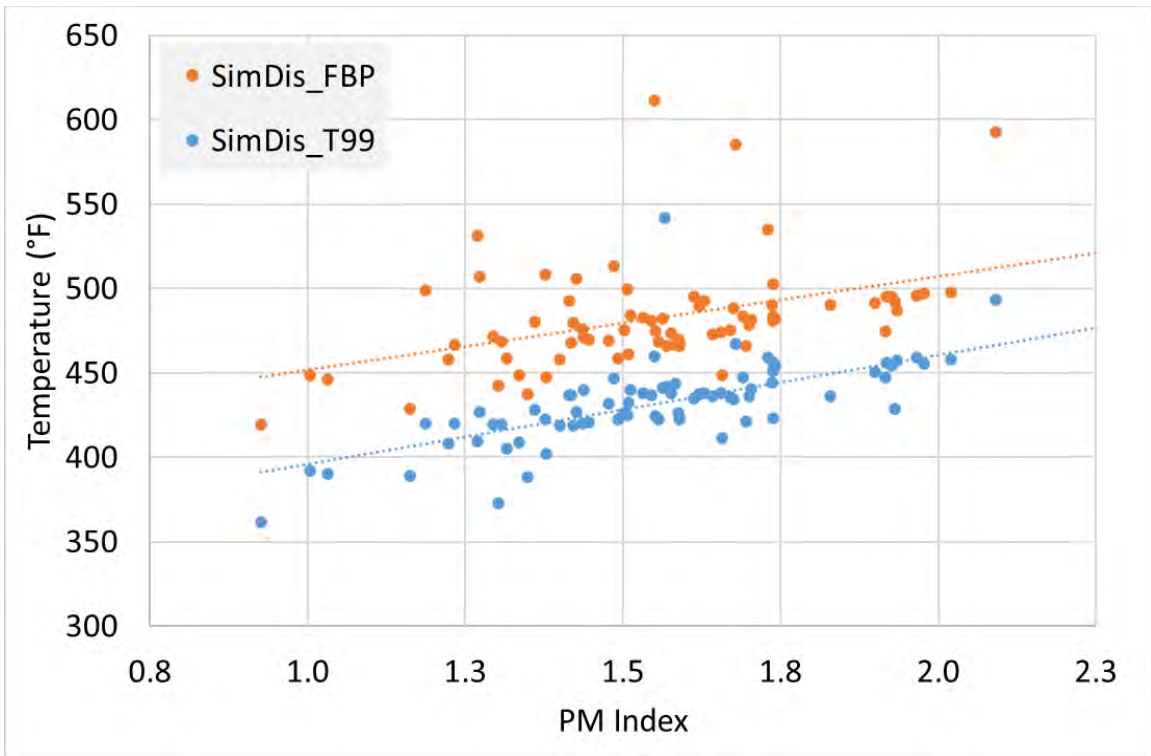


Figure 4.1. D7096 distillation profiles and PM Index values for four US market fuel samples.

Figure 4.2 and Figure 4.3 plot SimDis temperature versus PM Index for T95 through final boiling point (FBP). A positive correlation is clear for all the series plotted, with correlation appearing tightest for T97 and T98. Scatter expands markedly for the FBP series.



**Figure 4.2. Plot of SimDis T95-T98 temperature versus PM Index for 80 US market fuels.**



**Figure 4.3. Plot of SimDis T99 and final boiling point (FBP) temperature versus PM Index for 80 US market fuels.**

Table 4.1 shows a matrix of Pearson correlation coefficients for SimDis values T90 through T99. Correlation with PM Index is also shown in the first column, values that correspond to the two figures above. All distillation points from T90 to T99 exhibit reasonably good correlation to the PM Index, with T98 having the highest coefficient ( $\rho=0.832$ ) in the 80-sample study.

**Table 4.1. Pearson Correlation of Distillation Points vs PM Index for a dataset of 80 US market fuels.**

80 Samples	PMI(SwRIDHA)	T90	T91	T92	T93	T94	T95	T96	T97	T98	T99
PMI(SwRIDHA)	1										
T90	0.765	1									
T91	0.751	0.962	1								
T92	0.781	0.933	0.955	1							
T93	0.797	0.929	0.945	0.984	1						
T94	0.799	0.899	0.935	0.974	0.990	1					
T95	0.829	0.887	0.906	0.952	0.973	0.981	1				
T96	0.817	0.903	0.908	0.939	0.960	0.960	0.984	1			
T97	0.827	0.915	0.922	0.927	0.944	0.943	0.964	0.985	1		
T98	0.832	0.888	0.897	0.906	0.918	0.919	0.938	0.962	0.981	1	
T99	0.710	0.762	0.767	0.760	0.758	0.751	0.760	0.806	0.846	0.900	1



## 4.2 DHA and PMI Analysis

Table 4.2 and Table 4.3 summarize the PMI contribution and volume contribution from specific groups of compounds in the gasoline survey data. Since unidentified components can't be included in the PM Index calculation, they are not reported in Table 4.2. The volumes as identified from the DHAs are organized by temperature ranges, as defined in [14].

**Table 4.2. Average PMI% contribution by chemical groups in selected temperature ranges from DHA, where I is isoparaffins, A is aromatics, N is naphthene, O is olefins, and Ox is oxygenates and P is paraffins, and U is unidentified.**

T°C Range	0-110		110-111		111-135		135-145		145-150		150-182		182-221		221-420	
PMI%	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std
A	0.30	0.11	4.32	1.82	-	-	11.87	4.38	-	-	19.97	3.00	23.17	3.73	29.01	6.98
I	1.54	0.40	-	-	0.90	0.30	0.47	0.13	0.05	0.02	0.84	0.31	0.49	0.18	0.16	0.08
N	1.31	0.42	-	-	1.06	0.38	0.12	0.05	0.12	0.04	0.49	0.17	0.06	0.02	-	-
O	0.49	0.24	-	-	0.12	0.06	0.10	0.05	0.10	0.05	0.11	0.05	0.10	0.05	-	-
Ox	0.78	0.17	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P	0.56	0.16	-	-	0.19	0.06	-	-	-	-	0.31	0.11	0.24	0.12	0.63	0.31
U	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

There were on average about 1.3 v% of each sample unidentified in the DHA. Since there is no information for the unknown compounds, no DBE or boiling points can be assigned and contributions to PMI are ignored. (It should be noted that unidentified components are accounted in SimDis results.)

**Table 4.3. Average v% contribution by chemical groups in selected temperature ranges from DHA, where I is isoparaffins, A is aromatics, N is naphthene, O is olefins, and Ox is oxygenates and P is paraffins, and U is unidentified.**

T°C Range	0-110		110-111		111-135		135-145		145-150		150-182		182-221		221-420	
Vol%	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std
A	0.63	0.18	4.63	1.57	-	-	6.49	1.86	-	-	5.41	0.93	3.14	0.72	0.70	0.29
I	27.05	3.47	-	-	5.02	1.49	1.50	0.29	0.13	0.05	1.39	0.45	0.44	0.16	0.05	0.03
N	6.67	1.30	-	-	2.17	0.70	0.16	0.07	0.15	0.05	0.46	0.15	0.02	0.01	-	-
O	5.57	2.11	0.02	0.01	0.33	0.13	0.17	0.08	0.13	0.06	0.10	0.04	0.04	0.02	-	-
Ox	9.44	1.08	-	-	-	-	-	-	-	-	-	-	-	-	-	-
P	14.93	3.84	-	-	0.91	0.15	-	-	-	-	0.61	0.17	0.16	0.08	0.06	0.03
U	0.02	0.01	-	-	0.10	0.05	0.05	0.03	0.02	0.01	0.39	0.13	0.49	0.21	0.27	0.12

Figure 4.4 and Figure 4.5 summarize the data shown in the previous two tables. It makes clear that the heavy tails of market fuels are dominated by aromatics and therefore have strong leverage on the PMI value (blue bars), despite the fact that the contribution of this material to overall gasoline volume is very small (orange circles). Two specific observations are:

- Fuel components with boiling points >360°F account for over half of the PMI value, but only 5% of the volume.
- Fuel components with boiling points >430°F account for almost 30% of the PMI value, but only 1% of the volume.

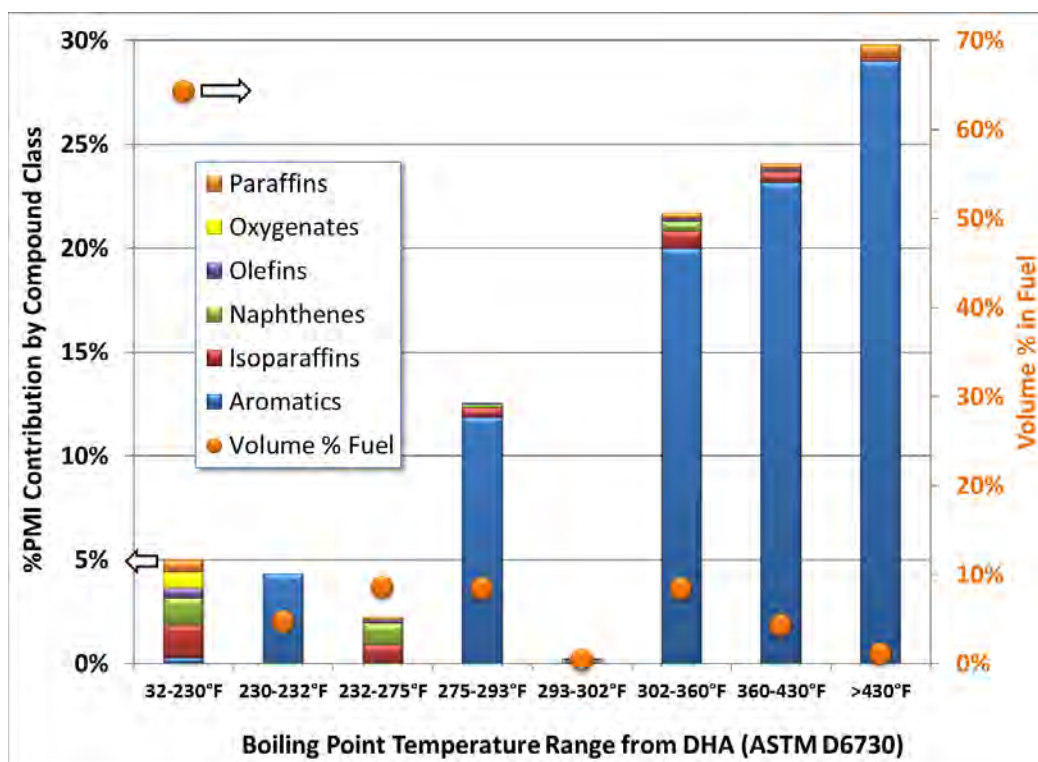


Figure 4.4. Percent PMI contribution by compound class and DHA-derived boiling point range.

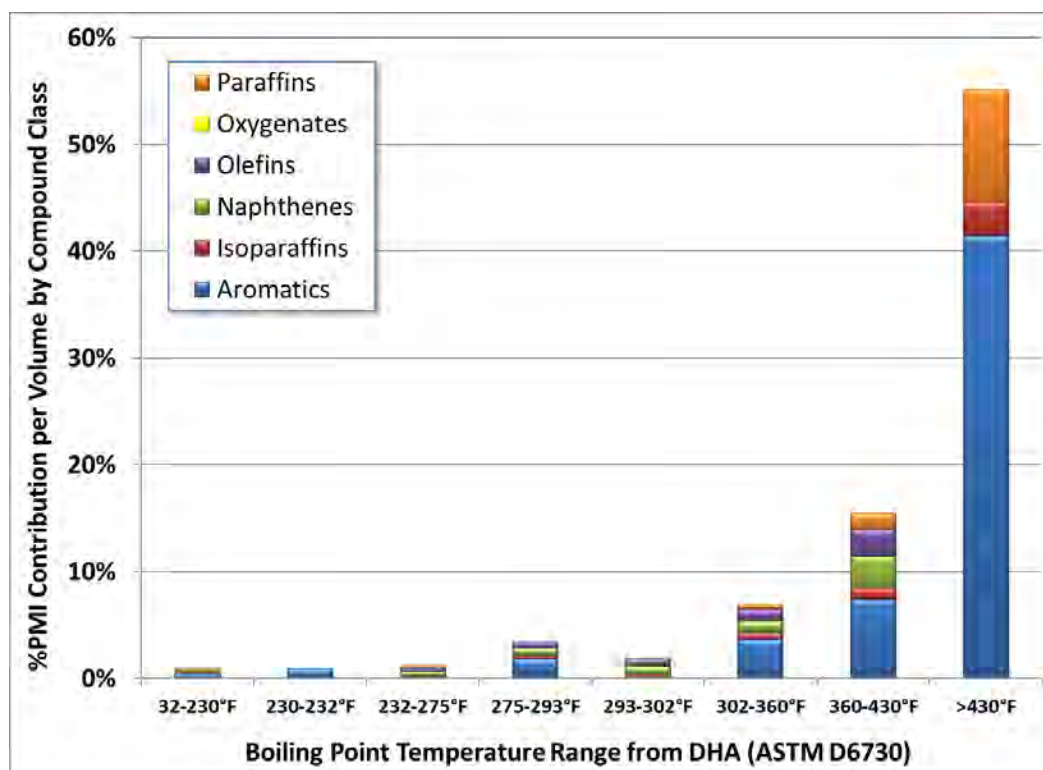


Figure 4.5. Percent PMI contribution per volume by compound class and DHA-derived boiling point range.

Further breakdown of aromatics by carbon number are presented in Table 4.4 and Table 4.5. Both PMI and volume percent are normalized from overall samples.

**Table 4.4. Average PMI contribution by aromatics by carbon number in selected temperature ranges from DHA.**

T°C Range	0-110		110-111		135-145		150-182		182-221		221-420	
	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std
PMI	0.005	0.001	-	-	-	-	-	-	-	-	-	-
A6	0.005	0.001	-	-	-	-	-	-	-	-	-	-
A7	-	-	0.066	0.022	-	-	-	-	-	-	-	-
A8	-	-	-	-	0.181	0.049	-	-	-	-	-	-
A9	-	-	-	-	-	-	0.271	0.046	-	-	-	-
A10	-	-	-	-	-	-	0.025	0.006	0.230	0.047	0.054	0.017
A11	-	-	-	-	-	-	0.004	0.002	0.112	0.035	0.187	0.086
A12	-	-	-	-	-	-	0.012	0.006	0.028	0.013	0.154	0.085
A13	-	-	-	-	-	-	-	-	-	-	0.053	0.026
A14	-	-	-	-	-	-	-	-	-	-	0.029	0.012

**Table 4.5. Average v% by aromatics by carbon number in selected temperature ranges from DHA.**

T°C Range	0-110		110-111		135-145		150-182		182-221		221-420	
	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std
Vol%	0.628	0.176	-	-	-	-	-	-	-	-	-	-
A6	0.628	0.176	-	-	-	-	-	-	-	-	-	-
A7	-	-	4.624	1.566	-	-	-	-	-	-	-	-
A8	-	-	-	-	6.488	1.857	-	-	-	-	-	-
A9	-	-	-	-	-	-	4.944	0.896	-	-	-	-
A10	-	-	-	-	-	-	0.355	0.083	2.104	0.423	0.124	0.039
A11	-	-	-	-	-	-	0.043	0.022	0.857	0.262	0.357	0.160
A12	-	-	-	-	-	-	0.065	0.034	0.172	0.076	0.176	0.093
A13	-	-	-	-	-	-	0.001	0.002	-	-	0.031	0.015
A14	-	-	-	-	-	-	-	-	-	-	0.008	0.004

Figure 4.6 summarizes the data shown in the two tables above. It is similar in format to Figure 4.4, but only the aromatic contribution is shown, and the aromatics are further grouped by carbon number (e.g., C10 means 10-carbon molecules). Aromatics boiling above 430°F—primarily C11 and above—account for 29% of the PMI value but only 0.7% of the fuel volume.

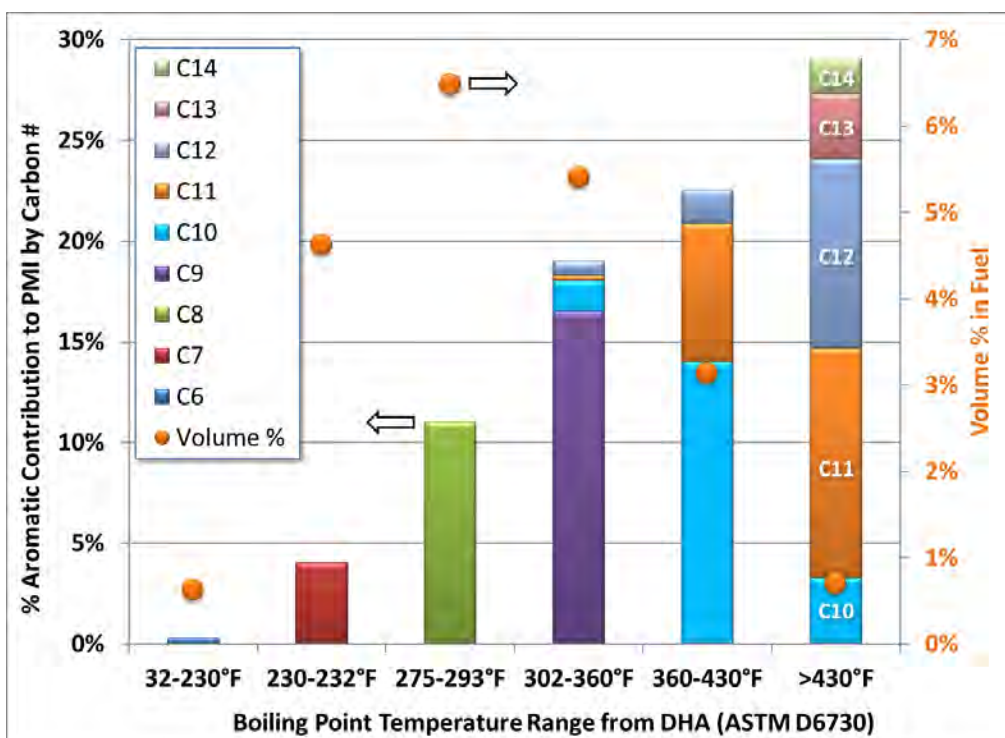


Figure 4.6. Percent aromatic contribution to PMI by carbon number and DHA-derived boiling point range.

### 4.3 SimDis Cut-Point Temperatures and PM Index Improvement in US Market Gasoline

The SimDis cut-off temperatures (endpoints or final boiling point limits) can be applied to the US market gasoline sample set as shown in Figure 4.7, Figure 4.9, and Figure 4.8. Based on the SimDis profiles, the targeted cut temperatures are defined and PM index is then adjusted using the DHA data after removing the cut off volume as described by Sobotowski, *et al.* [15].<sup>2</sup> The adjusted PMI can then be plotted with cut temperatures as shown in Figure 4.7 and Figure 4.8. The data points on the graph indicate the cut-off (or trim) volumes. Distributions of adjusted PMI are presented in Figure 4.9.

As shown in Table 4.5, the heavy ends are comprised mostly of aromatic compounds. As a result, reduction of PMI with minimum removal of heavy ends can be achieved. It should be noted that the DHA method typically leaves 0.5 to 0.8 v% reported as unidentified, meaning those compounds not included in the computation of PMI. However, their contribution to the heavy tail and PM formation is captured by SimDis.

<sup>2</sup> This analysis does not reflect reformulation of the remaining fuel volume to make up for loss of octane in material that was trimmed out. Octane make-up would be expected to produce a small reduction in the PMI impact shown. More detail is available in Sobotowski, et al. [15]

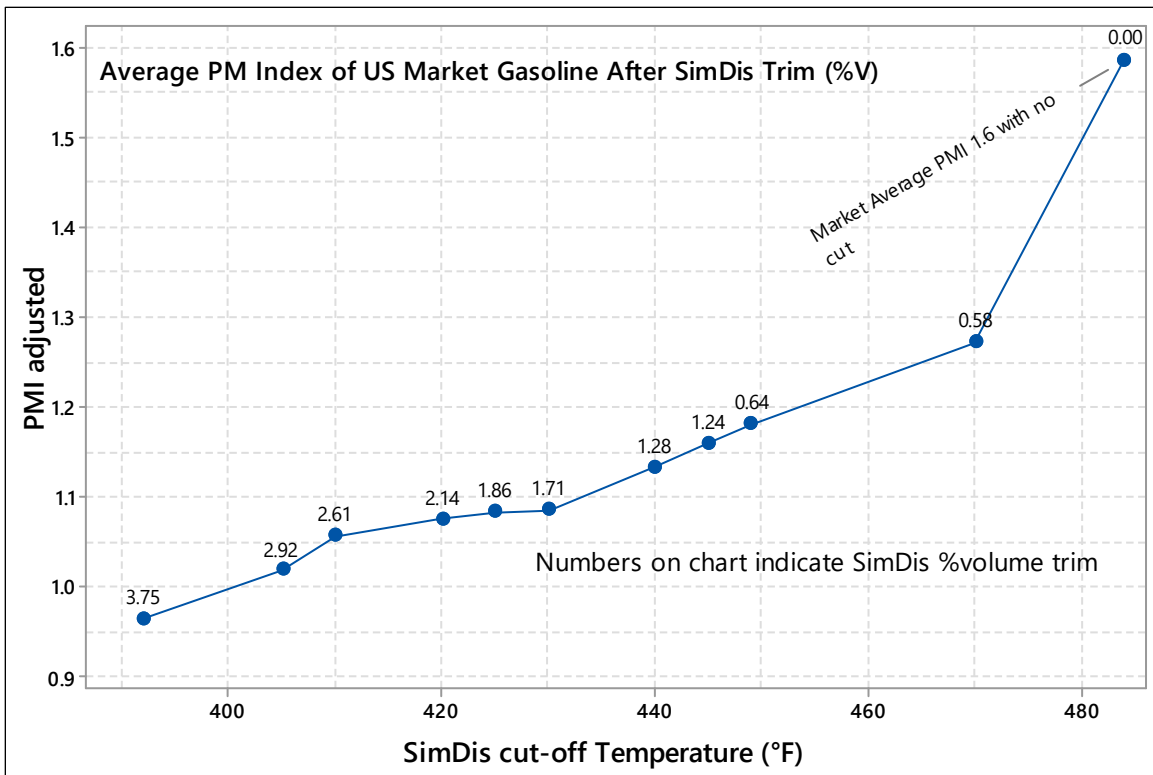


Figure 4.7. Estimated average PM Index adjustment of US market gasoline after SimDis cut-points.

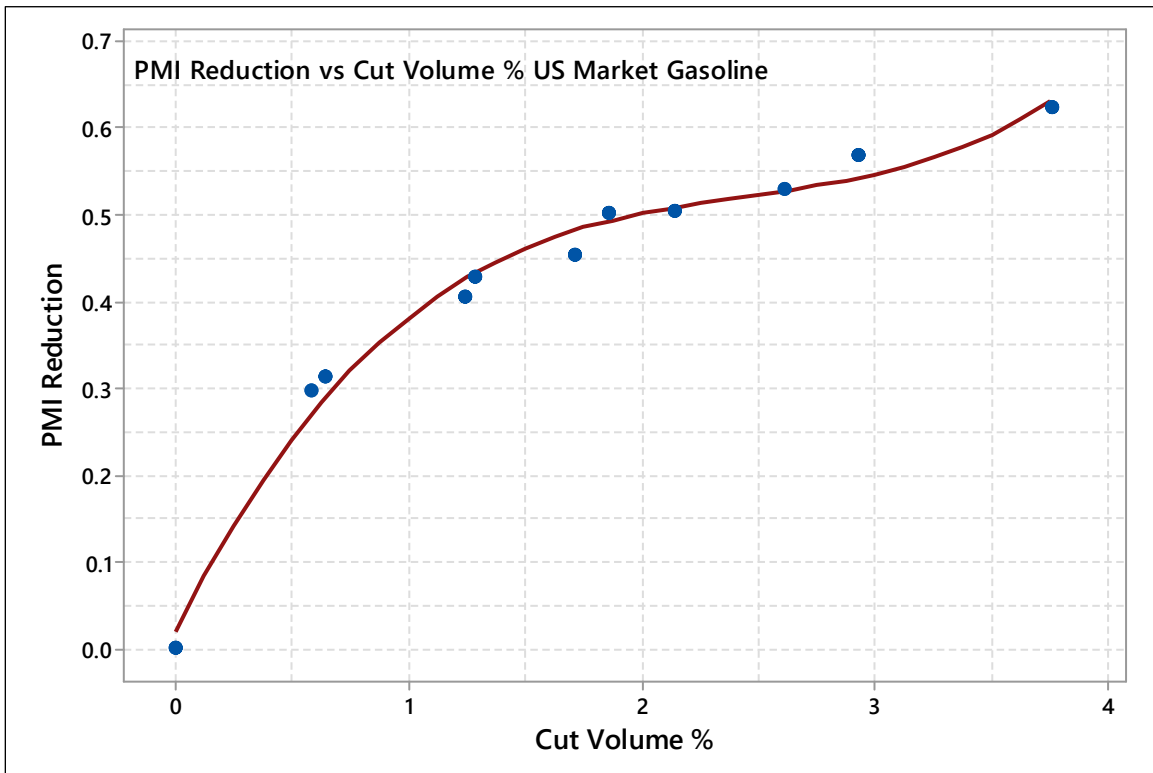
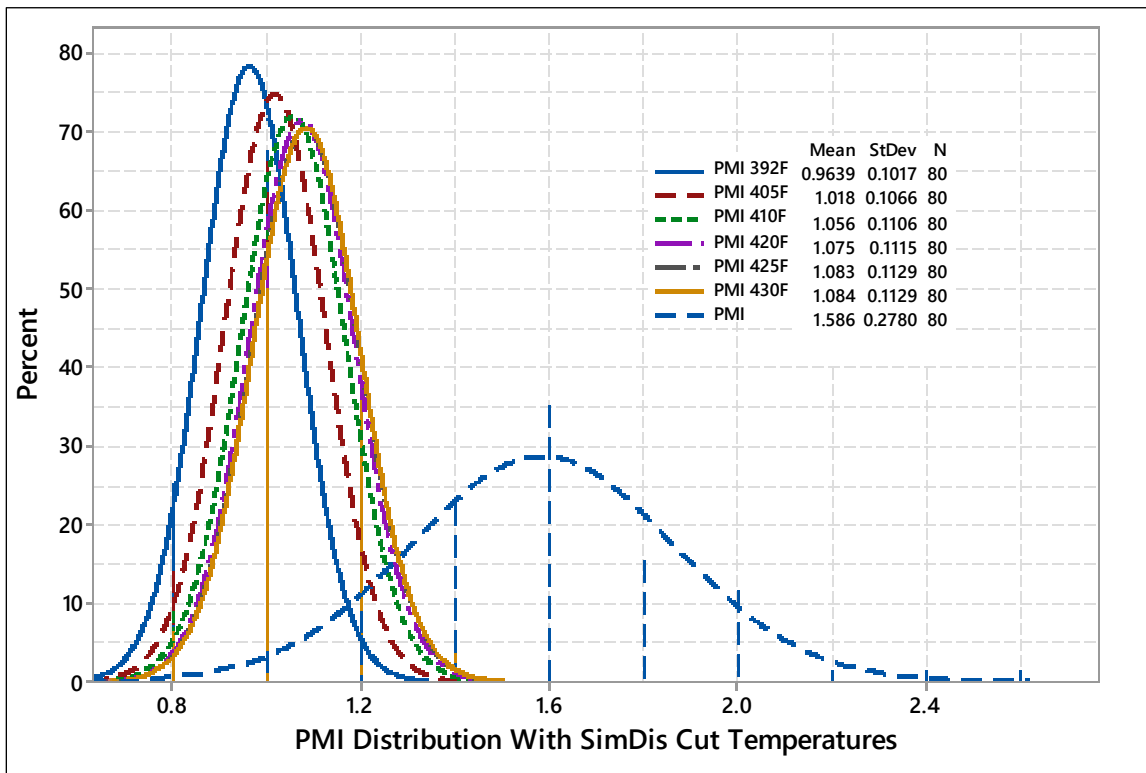


Figure 4.8. Estimated PM Index reduction of US market gasoline after SimDis cut-points.

Figure 4.9 shows the distribution of PMI values across the 80-sample market fuel survey before and after application of several SimDis FBP limits. PMI 392 denotes adjusted PMIs of samples with a SimDis cut-point temperature of 392°F, PMI 405 denoting adjusted PMIs of samples with a SimDis cut-point temperature of 405°F, etc.



**Figure 4.9. Distribution of adjusted PMI of US gasoline after SimDis cut-points.**

Starting from the survey sample average PMI of 1.6, this analysis indicates that a reduction in the market average PMI of 0.5 could be achieved by applying a SimDis FBP limit of 430°F, which would correspond to removing the heaviest 1.7 v% of the average gasoline sample.

## 5. Summary and Conclusions

ASTM D7096 SimDis is a gas-chromatography method that provides a relatively precise volatility profile of a gasoline sample. Detailed hydrocarbon analysis (DHA) of market gasoline shows that the high-boiling tail is comprised primarily of aromatics that have high leverage on PM emissions. Thus, quantification of high-boiling material by SimDis could be a useful surrogate for DHA-based parameters such as PM Index if good repeatability and correlation can be demonstrated.

This work explored sources of variability in SimDis results and developed several procedural recommendations to improve repeatability and reproducibility within the method as written, focusing on the high-boiling (T90+) tail of gasoline. Validation studies done at EPA and GM laboratories showed that reproducibility values well below those published by ASTM can be achieved.

Following the method improvement work, SimDis as well as ASTM D6730 DHA were run on 80 gasoline samples taken from the US market in 2021-22. Contribution to PM Index and volume percent was assessed by boiling range and molecular class. This analysis shows that the heavy tail of gasoline contains a large proportion of aromatics that have high leverage on PM Index, findings that are consistent with previous work [12]. Correlation between PM Index values and a range of heavy-end SimDis T-numbers (or %-off values) was also assessed. Results indicated that the highest correlation occurred in the range of SimDis T95-T98 with a Pearson coefficient around 0.83.

Finally, the impact on PM Index of applying several SimDis cut-points (or endpoints) to trim heavy-end material from market gasoline was assessed. Starting from the survey sample average PMI of 1.6, this analysis suggests a PMI reduction of 0.5 (31%) could be achieved by applying a SimDis final boiling point limit of 430°F. This would correspond to removing the heaviest 1.7 v% of the average market fuel, and supports the conclusion that a relatively large reduction in PM Index could be achieved with removal of a small amount of high-boiling material from gasoline.

## Acknowledgement

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## **APPENDIX A:**

# **Simulated Distillation for Heavy Aromatics Laboratory Procedure**

**Version – 01**

**1. Scope**

This method is based off ASTM test method D7096<sup>1</sup>, and is intended to measure the distillation curves of gasoline and gasoline-ethanol blends with a boiling point range within that of nC3 – nC16 hydrocarbons. This method further specifies analytical conditions set forth in ASTM D7096 with the goal of increasing the interlaboratory analytical precision.

**2. Summary of Method**

This method uses a wide bore non-polar GC column to separate gasoline samples according to boiling point. Retention times and response factors of a calibration sample are used to calculate the volume percent eluted at a given time - and by extension boiling point. Cumulative volume percent and boiling temperature are plotted to yield a distillation curve.

**3. Significance**

**4. Definitions**

*control sample* - a reference gasoline sample is used to verify both the chromatography and calculation process

*final boiling point* – the point at which the cumulative volume counts is equal to 99.5 % of the total volume counts under the chromatogram is obtained

*initial boiling point* - the point at which the cumulative volume counts is equal to 0.5 % of the total volume counts under the chromatogram is obtained

**5. Interferences and/or Limitations**

Ethanol/oxygenates response factors are known to differ significantly from other gasoline components. The presence of high amounts of oxygenates is likely to interfere with accurate volume estimation. Samples up to 10% ethanol have been analyzed by this method without undue bias. The bias imposed by other oxygenates and increased ethanol content have not been investigated.

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<sup>1</sup> ASTM Standard D7096, 2016, “Standard Test Method for the Determination of the Boiling Range Distribution of Gasoline by Wide-Bore Capillary Gas Chromatography”, ASTM International, West Conshohocken, PA, 2016, DOI: 10.1520/D7096-16.

**6. Apparatus**

Agilent gas chromatograph (GC) equipped with an flame ionization detector (FID) and a 30 m x 0.53 mm 100 % polydimethylsiloxane (PDMS) column film thickness of 5 µm (or comparable column with equivalent stationary phase and length) is used in this test procedure.

Chemstation software is used for data acquisition. Separation Systems, Inc. SimDis Expert 10 (or equivalent software package capable of automating the necessary calculations) is used for data analysis.

Sample introducing systems (autosampler, microliter syringe and injection port) capable of introducing 1.0 µL into the split inlet device of the gas chromatograph.

**Equipment Maintenance:**

In response to problems with instrument functionality or out-of-tolerance events, a number of local maintenance or troubleshooting activities may be performed to resolve the problem. These include the investigation of:

Auto Sampler	Power Supply	Computer
Mobile Phase	Performance Test Mixture Integrity	Reagent Purity
Instrument Setup	Data Entry	Sample Integrity
Injector Valve	Detector	Analytical Column
Sampling Needle	Temperature Controller	Pressure Controller
Sampling Loop		

**7. Reagents and Materials**

- 2-mL GC sample vials and aluminum crimp caps with rubber septa are used as samples containers for the auto-sampler.
- Disposable glass transfer pipettes are used to transfer samples GC sample vial.
- Standardization Standard mixtures can be purchased and should span the nC3 – nC16 hydrocarbon boiling range and include several aromatic compounds in that boiling range.
- calibration standard – a mixture of pure hydrocarbons that possess boiling points over the range of that expected for the samples (i.e. C3 – C 16). A single calibration standard may be used for both, retention time calibration and relative response factor validation. It is necessary to know the identity and amount of each component in the calibration standard.
- calibration standard with oxygenates – in the event that samples contain oxygenates, the calibration standard shall also contain the oxygenates, in addition to the hydrocarbons. The concentration of each oxygenate in the calibration standard should approximate that of samples.

- control sample – with each batch (see 9.3) of samples analyzed, a reference gasoline sample should be analyzed, allowing for verification of system integrity. This sample should be available in relatively large quantity and be similar in composition to fuels regularly analyzed.

## 8. Sampling

Samples should be cold (0 – 4 °C) when transferring.

Fuel is sampled by pipetting into a 2 mL crimp-top vial with PTFE-lined septa to 90% maximum volume.

When transporting fuel for analysis, samples should be transported in volumes of 1 L or greater.

## 9. Analytical Procedure

### 9.1 Sample Handling:

Sample handling is critical to achieving acceptable repeatability and reproducibility. Whenever possible, efforts should be taken to decrease potential loss of high volatility sample components. This includes storing and aliquoting samples cold, minimizing storage container and sample vial headspace, limiting sample exposure to heat sources and ensuring proper sealing of all closures. When a sample needs to be stored for a long period it is best to do so with a large (e.g. 1 L) container.

### 9.2 Operating Conditions:

The GC operating conditions are:

Oven: 40 °C 1 min, 25 °C/min to 260 °C, 4 min hold 6 min post run @40 °C

Injection Volume: 1 µL

Wash 6X DCM (or CS<sub>2</sub>), 6X CS<sub>2</sub>

Injection: 300 °C, Split 50:1, Focus liner w/glass wool

Carrier Gas: He, 5 mL/min for 0.6 min, 30 mL/min<sup>2</sup> to 20 mL/min

Detector: FID, 300 °C, 30 ml/min combined makeup

### 9.3 Batch Order:

A sample batch should include standards, blanks and samples in the following injection order, repeating 6 and 7 as needed according to the number of samples to be analyzed:

1. System Blank (repeat 3 times)
2. Standard
3. Solvent Blank (CS<sub>2</sub>, repeat 2 times)
4. Control Sample
5. Solvent Blank (CS<sub>2</sub>, repeat 2 times)

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6. Sample
7. Solvent Blank (CS2, repeat 2 times)
8. Control Sample

#### **9.4 Calibration**

*Retention Time Calibration* - Prior to the analysis of samples, a calibration must be performed, defining the correlation between retention time and boiling point. Calibration is performed by analyzing a mixture of known hydrocarbons covering the boiling point range expected. For samples containing oxygenates, the retention time calibration mixture must contain those oxygenates.

### **10. Processing, Calculations, and Reporting**

#### **10.1 Sample Calculations**

Sample calculations are carried out automatically by post-processing software. The third system blank of the batch should be used for baseline correction of all subsequent samples. Report volume percent data in 0.5 °C increments and include initial and final boiling points.

#### **10.2 QC Evaluation**

QC sample: Use ASTM r to compare repeatability.

Calibration performance: Use relative volume response factor (measured) and compare to relative volume response factor (theoretical). Values should agree to within 10% of theoretical values. Refer to ASTM D7096 for resolution, column selectivity and peak skewing.