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# Evaluation of Alternative Methods to Measure Aromatic Content of Aviation Fuels

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## List of Symbols, Abbreviations, and Acronyms

| | |
|---|---|
| AFPET | Air Force Petroleum Office |
| AFRL | Air Force Research Laboratory |
| CCDC | Combat Capabilities Development Command |
| CHCJ-5 | Catalytic Hydrothermal Conversion-to-Jet |
| DOD | Department of Defense |
| F-24 | Jet-A fuel with military additives |
| GC-FID | Gas Chromatography – Flame Ionization Detector |
| GC-VUV | Gas Chromatography – Vacuum Ultraviolet spectroscopy |
| GVSC | Ground Vehicle Systems Center |
| ILS | Interlaboratory Study |
| HEFA | Hydroprocessed Esters and Fatty Acids |
| Jet A-1 | Commercial Jet Propellant with a freeze point of minus 47ºC or below |
| JP-5 | Jet Propellant 5 |
| JP-8 | Jet Propellant 8 |
| NAVAIR | Naval Air Systems Command |
| R | Reproducibility |
| r | Repeatability |
| SwRI | Southwest Research Institute |
| TRIPOL | Tri-Service Petroleum, Oil, and Lubricants |

## 1. Introduction

For decades, the fuel industry has relied on ASTM D1319, *Standard Test Method for Hydrocarbon types in Liquid Petroleum Products by Fluorescent Indicator Adsorption* [1], to quantify the aromatic content of aviation (jet), diesel, and gasoline fuels. In 2018, Honeywell UOP was forced to change the fluorescent indicator dye gel formulation in response to the olefin marker component no longer being available. Honeywell UOP selected a new olefin marker without notification to the users or ASTM International. Industry users of this newly formulated dye, specifically gasoline users, found that the new dye was not fluorescing as intensely as previous dye lots and raised concerns. Honeywell UOP then identified the change to the dye. ASTM Subcommittees A (gasoline), E (diesel) & J (jet) issued ballots stating that dye lots 3000000975 through 3000000980 were not to be used to report results for aromatic content testing in specifications ASTM D4814, ASTM D975, and ASTM D1655 respectively.

In response, the DOD needed to determine if alternative methods could be used as a replacement for ASTM D1319 to measure aromatics to mitigate risk in the event Honeywell UOP could not find a suitable dye formulation. ASTM D6379, *Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates – High Performance Liquid Chromatography with Refractive Index Detection* [2], and ASTM D5186, *Determination of Aromatic Content and Polynuclear Aromatic Content of Diesel and Aviation Turbine Fuels by Supercritical Fluid Chromatography* [3] were identified as potential replacement methods to be examined and compared to ASTM D1319. Since the testing commenced, ASTM International published ASTM D8305, *Standard Test Method for The Determination of Total Aromatic Hydrocarbons and Total Polynuclear Aromatic Hydrocarbons in Aviation Turbine Fuels and other Kerosene Range Fuels by Supercritical Fluid Chromatography* [4], and revised ASTM D5186* to remove aviation fuels. This new test method, ASTM D8305, includes the modified D5186 protocol that was used during this study. Collaboration between the Army, Air Force, Navy, and Southwest Research Institute (SwRI), showed that the DOD had the testing capabilities to compare the accuracy, repeatability, and reproducibility of all three methods. The data collected from this study was presented at the June 2019 ASTM International D02 meeting in Denver, Colorado.

Concurrently, Honeywell UOP presented on a new formulation of the dye gel, showing this new olefin marker was chemically similar to the discontinued olefin marker [5]. ASTM International Subcommittee D02.04.0C on Liquid Chromatography also presented on the status of the Interlaboratory Study (ILS) planned to test the new formulation of the dye gel [6]. However, the DOD Tri-Service POL Users Group felt the study would not be conducted in a timely manner, and a decision regarding the acceptability of the new dye gel lot was needed sooner to maintain DOD operational readiness. The DOD completed testing on the new dye and has recently published their findings [7].

## 2. Approach

US Army Combat Capabilities Development Command (CCDC) Ground Vehicle System Center (GVSC), Naval Air Systems Command (NAVAIR), Air Force Petroleum Office (AFPET), Air Force Research Laboratory (AFRL) and Southwest Research Institute (SwRI) agreed to participate in the comparison of ASTM D1319-18, ASTM D5186-15*, and ASTM D6379-11.

Each of the laboratories possessed different testing capabilities and are listed in Table 3. GVSC coordinated the testing program, collected, and analyzed the data for the study. AFRL distributed 12 jet fuel samples ranging in aromatic content from 0-24 vol %, previously measured using ASTM D1319, to each laboratory. Sample information can be found in Table 1. GVSC prepared the testing protocol to ensure each laboratory conducted the tests in the same manner. The protocol can be found in Appendix A.

**Table 1.** DOD Aromatics Round Robin - Sample Information

| | |
|---|---|
| **Laboratories** | 5 |
| **Samples** | 12 jet fuels; 0-24% aromatics:<br>4, F-24<br>3, JP-8<br>2, JP-5<br>1, Jet A-1<br>1, CHCJ-5<br>1, HEFA |
| **Data Points*** (gathered in duplicate) | |
| ASTM D1319-18 | 72* |
| ASTM D5186-15 | 48 |
| ASTM D6379-11 | 72* |
| *Data points were omitted from the study if they did not conform to the statistical analysis protocol outlined in ASTM E691-18. | |

**Table 2.** Participating Laboratories

| | ASTM D1319-18 | ASTM D5186-15* | ASTM D6379-11 |
|---|---|---|---|
| **DOD 1** | X | | X |
| **DOD 2** | X | X | |
| **DOD 3** | | | X |
| **DOD 4** | | X | |
| **DOD 5** | X | | X |
| *ASTM D5186-15 used a modified protocol provided by Selerity Technologies that matches ILS (WK48207) conducted in Feb 2019. At time of testing, DOD labs used the modified ASTM D5186-15 protocol which has since been incorporated into a new test procedure, ASTM D8305, which was validated by ILS (WK48207). The Selerity ILS was run to be compliant with ASTM D5186-15 with modified cut times to improve the precision for aviation turbine fuels per the Dec 2018 ASTM meeting. | | | |

Each laboratory conducted testing on the 12 jet fuels samples in duplicate. ASTM D1319-18 and D6379-11 was conducted in 3 laboratories producing an initial 72 data points. Data points were omitted from the study if they did not conform to the statistical analysis protocol outlined in ASTM E691-18, *Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method* [8]. Statistical analysis was conducted and the averages, standard deviations, repeatability, and reproducibility were reported. The testing was conducted 2 February 2019 through 22 April 2019, and all data was submitted to GVSC by 23 April 2019.

## 3. Evaluation and Analysis

**Table 3.** Methodology Comparison of ASTM D1319-18, D5186-15*, and D6379-11

| | **ASTM D1319-18** | **ASTM D5186-15*** | **ASTM D6379-11** |
|---|---|---|---|
| **Testing Type** | Fluorescent Indicator Adsorption | Supercritical Fluid Chromatography | High Performance Liquid Chromatography |
| **Hydrocarbon Types** | Olefins, Aromatics, Saturates | Di-aromatics, Mono-aromatics, Non-aromatic hydrocarbons | Mono-aromatics, Non-aromatics, Poly-nuclear aromatics |
| **Reporting Units** | Vol % | Mass % | Mass % |
| **Supported Distillate Boiling Range** | Below 315°C | Not Specified | 50 - 300°C |
| **Calibration** | Not calibrated; visual measurement | Calibrated; Vol % or Mass % | 4 calibrating verifications are performed |

In review of each test method and depicted in Table 3, differences exist in how each method tests, reports, and defines aromatic content in fuel. Additionally, aromatic content is calculated differently by equations found in their respective test methods. ASTM D1319-18 employs a more manual approach utilizing adsorption columns whereas ASTM D5186-15* and ASTM D6379-11 use chromatography via an automatic instrument. Aromatic content is reported consistently to the nearest 0.1% for each method, however, the reporting units differ from vol % to mass %. Calibration procedures also vary between the methods. Both ASTM D5186-15* and ASTM 6379-11 have some form of calibration protocol for their respective instruments whereas ASTM D1319-18 does not.

## Statistics - Repeatability & Reproducibility

**Table 4.** Repeatability and Reproducibility Metrics for ASTM D1319-18, D5186-15*, and D6379-11

| | ASTM D1319-18 | ASTM D5186-15* | ASTM D6379-11 |
|---|---|---|---|
| **Repeatability (r)** | No Equation; Section 13, Table 3 for Oxygenate Free Samples (Vol %) | Equation; Section 13.1.1 based on Di, Mono, and Total aromatics (Mass %) | Equation; Section 13.1.1 based on Poly-nuclear and Total aromatics (Mass %) |
| **Reproducibility (R)** | No Equation; Section 13, Table 3 for Oxygenate Free Samples* (Vol %) | Equation; Section 13.1.2 based on Di, Mono, and Total aromatics* (Mass %) | Equation; Section 13.1.2 based on Poly-nuclear and Total aromatics* (Mass %) |

Table 4 shows the differences between each methods respective repeatability and reproducibility metrics. ASTM D5186-15* and D6379-11 both utilize equations based off the detected aromatic content to determine repeatability and reproducibility whereas ASTM D1319-18 have correlating tables (Tables 3 & 4) for either oxygenated or non-oxygenated fuels.

**Table 5.** ASTM D1319-18 Reproducibility Metrics – Total Aromatics (vol %)

| Sample | Reproducibility from ASTM D1319-18 Table 3 | DOD 1 Aromatic Content Mean | DOD 2 Aromatic Content Mean | Absolute Difference | Met Reproducibility |
|---|---|---|---|---|---|
| 1 | 2.5 | 11.1 | 11.4 | 0.3 | Yes |
| 2 | 3.0 | 21.0 | 20.7 | 0.3 | Yes |
| 3 | 2.5 | 14.0 | 14.2 | 0.2 | Yes |
| 4 | 3.0 | 19.8 | 19.8 | 0 | Yes |
| 5 | 3.0 | 20.2 | 19.3 | 0.9 | Yes |
| 6 | 2.5 | 15.0 | 15.4 | 0.4 | Yes |
| 7 | 2.5 | 10.8 | 10.7 | 0.1 | Yes |
| 8 | 2.5 | 11.9 | 11.2 | 0.7 | Yes |
| 9 | 3.0 | 18.3 | 18.2 | 0.1 | Yes |
| 10 | 3.0 | 18.7 | 18.5 | 0.2 | Yes |
| 11 | 3.0 | 15.8 | 16.4 | 0.6 | Yes |
| 12 | 1.5 | 0.7 | 0.7 | 0 | Yes |

ASTM D1319-18 was performed on 12 samples in three laboratories for a total of 72 data points. However, DOD 5 did not run ASTM D1319-18 in duplicate in accordance with ASTM E691-18 and therefore was omitted from the study. The means calculated in Table 5 were derived from the two data points acquired by each lab, for each sample. All samples fell within their respective reproducibility ranges as stated in Table 3 of ASTM D1319-18. All raw data can be found in Appendix B.

**Table 6.** ASTM D5186-15* Reproducibility Metrics – Total Aromatic (vol %)

| Sample | Reproducibility from ASTM D5186-15* | DOD 2 Aromatic Content Mean | DOD 4 Aromatic Content Mean | Absolute Difference | Met Reproducibility |
|---|---|---|---|---|---|
| 1 | 1.4 | 11.7 | 11.5 | 0.2 | Yes |
| 2 | 1.6 | 20.7 | 20.3 | 0.4 | Yes |
| 3 | 1.4 | 14.1 | 13.9 | 0.2 | Yes |
| 4 | 1.5 | 19.5 | 19.1 | 0.4 | Yes |
| 5 | 1.6 | 20.0 | 19.7 | 0.3 | Yes |
| 6 | 1.5 | 15.6 | 15.4 | 0.2 | Yes |
| 7 | 1.3 | 10.9 | 10.7 | 0.2 | Yes |
| 8 | 1.4 | 12.4 | 12.1 | 0.3 | Yes |
| 9 | 1.5 | 17.4 | 17.1 | 0.3 | Yes |
| 10 | 1.5 | 18.9 | 18.7 | 0.3 | Yes |
| 11 | 1.5 | 15.8 | 15.6 | 0.2 | Yes |
| 12 | 0.6 | 0.4 | 0.3 | 0.1 | Yes |

ASTM D5186-15* was performed on 12 samples in two laboratories for a total of 48 data points. The means calculated in Table 6 were derived from the two data points acquired by each lab, for each sample. A bias correction was applied to the data as stated in ASTM D8305 while being compared to data from ASTM D1319-18. All samples fell within their respective reproducibility ranges as stated in section 13 of ASTM D5186-15*. All raw data can be found in Appendix B.

**Table 7.** ASTM D6379-11 Precision Statistics – Total Aromatics (vol %)

| Sample | Reproducibility from ASTM D6379-11 | DOD 1 Aromatic Content Mean | DOD 3 Aromatic Content Mean | Absolute Difference | Met Reproducibility |
|---|---|---|---|---|---|
| 1 | 1.5 | 11.4 | 11.2 | 0.2 | Yes |
| 2 | 2.4 | 23.3 | 22.4 | 0.9 | Yes |
| 3 | 1.8 | 16.0 | 15.3 | 0.7 | Yes |
| 4 | 2.2 | 20.3 | 19.5 | 0.8 | Yes |
| 5 | 2.2 | 20.1 | 19.6 | 0.5 | Yes |
| 6 | 1.9 | 16.1 | 15.2 | 0.9 | Yes |
| 7 | 1.5 | 11.3 | 10.6 | 0.7 | Yes |
| 8 | 1.6 | 12.0 | 11.4 | 0.6 | Yes |
| 9 | 2.1 | 20.2 | 19.2 | 1.0 | Yes |
| 10 | 2.2 | 19.9 | 18.8 | 1.1 | Yes |
| 11 | 2.0 | 17.9 | 16.6 | 1.3 | Yes |
| 12 | 0.1 | 0.1 | 0.1 | 0 | Yes |

ASTM D6379-11 was performed on 12 samples in three laboratories for a total of 72 data points. However, DOD 5 did not meet the requirements for interlaboratory repeatability in accordance with ASTM E691-18 and therefore was omitted from the study. The means calculated in Table 7 were derived from the two data points for each sample. All samples fell within their respective reproducibility ranges as stated in section 13 of ASTM D6379-11. All raw data can be found in Appendix B.

## Statistics – Total Aromatic Content Comparisons

**Table 8.** Total Aromatic Content Comparison between ASTM D1319-18, D5186-15*, and D6379-11

| Sample | ASTM D1319-18 | | | ASTM D5186-15* | | | ASTM D6379-11 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Data Points | Mean | Standard Deviation | Data Points | Mean | Standard Deviation | Data Points | Mean | Standard Deviation |
| 1 | 11.4, 10.8, 11.2, 11.6 | 11.2 | 0.447 | 11.7. 11.7, 11.7, 11.4 | 11.6 | 0.127 | 11.6, 11.3, 11.2, 11.2 | 11.3 | 0.189 |
| 2 | 20.5, 20.9, 20.6, 21.3 | 20.8 | 1.021 | 20.7, 20.7, 20.4, 20.3 | 20.5 | 0.222 | 23.4, 22.3, 22.3, 22.5 | 22.9 | 0.556 |
| 3 | 14.1, 14.2, 14.0, 14.0 | 14.1 | 0.096 | 14.1, 14.1, 13.9, 13.8 | 14.0 | 0.162 | 16.2, 15.9, 15.2, 15.4 | 15.7 | 0.457 |
| 4 | 19.1, 20.5, 19.8, 19.8 | 19.8 | 0.730 | 19.4, 19.5, 19.1, 19.1 | 19.3 | 0.222 | 20.3, 20.3, 19.3, 19.8 | 19.9 | 0.478 |
| 5 | 19.3, 19.2, 20.4, 20.0 | 19.7 | 0.632 | 20.0, 20.0, 19.7, 19.8 | 19.9 | 0.174 | 20.1, 20.1, 19.6, 19.6 | 19.8 | 0.288 |
| 6 | 15.4, 15.3, 14.8, 15.2 | 15.2 | 0.434 | 15.6, 15.6, 15.5, 15.3 | 15.5 | 0.120 | 16.2, 16.1, 15.0, 15.5 | 15.7 | 0.559 |
| 7 | 10.7, 10.6, 10.7, 10.9 | 10.7 | 0.493 | 11.0, 10.9, 10.7, 10.7 | 10.8 | 0.127 | 11.4, 11.3, 10.7, 10.5 | 11.0 | 0.442 |
| 8 | 11.3, 11.0, 11.9, 11.9 | 11.5 | 0.416 | 12.4, 12.3, 12.1, 12.2 | 12.3 | 0.154 | 12.1, 12.0, 11.5, 11.4 | 11.7 | 0.351 |
| 9 | 17.9, 18.4, 18.7, 17.8 | 18.2 | 0.370 | 17.4, 17.3, 17.1, 17.2 | 17.2 | 0.154 | 20.3, 20.2, 19.2, 19.3 | 19.7 | 0.580 |
| 10 | 18.3, 18.6, 18.8, 18.5 | 18.6 | 0.545 | 18.9, 18.9, 18.7, 18.7 | 18.8 | 0.127 | 20.0, 19.8, 18.7, 19.0 | 19.4 | 0.623 |
| 11 | 16.4, 16.4, 16.1, 15.4 | 16.1 | 0.550 | 15.8, 15.8, 15.6, 15.5 | 15.7 | 0.162 | 18.0, 17.9, 16.5, 16.8 | 17.3 | 0.761 |
| 12 | 0.7, 0.6, 0.7 0.7 | 0.7 | 0.055 | 0.3, 0.3, 0.4, 0.3 | 0.3 | 0.069 | 0.2, 0.1, 0.1, 0.1 | 0.1 | 0.050 |

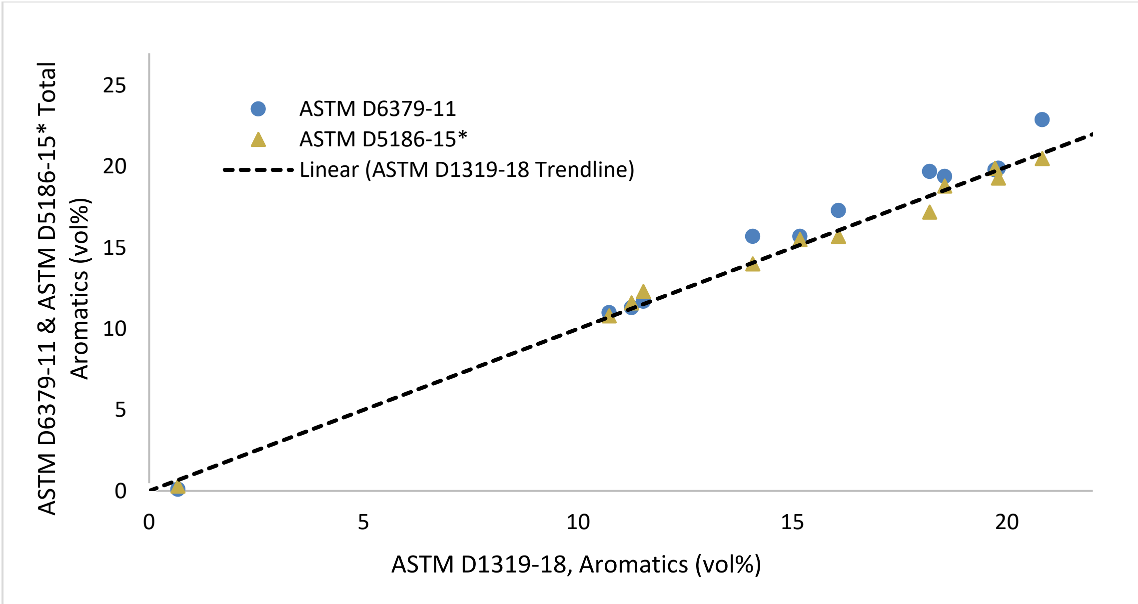


**Figure 1.** Total Aromatic Content Correlation

ASTM D5186-15* and ASTM D6379-11 data was plotted against D1319-18 data, and the trendline depicts the agreement among the data sets. ASTM D5186-15* and ASTM D6379-11 data was converted to vol % for comparison to ASTM D1319-18 data using the mathematical process highlighted in ASTM D6379-11. In this approach the density of a mono-aromatic standard (o-xylene, 0.88 g/mL) and a diaromatic standard (1-methylnaphthalene, 1.0 g/mL) are used to scale the fuel density for the respective aromatic fraction when converting from mass % to vol %.

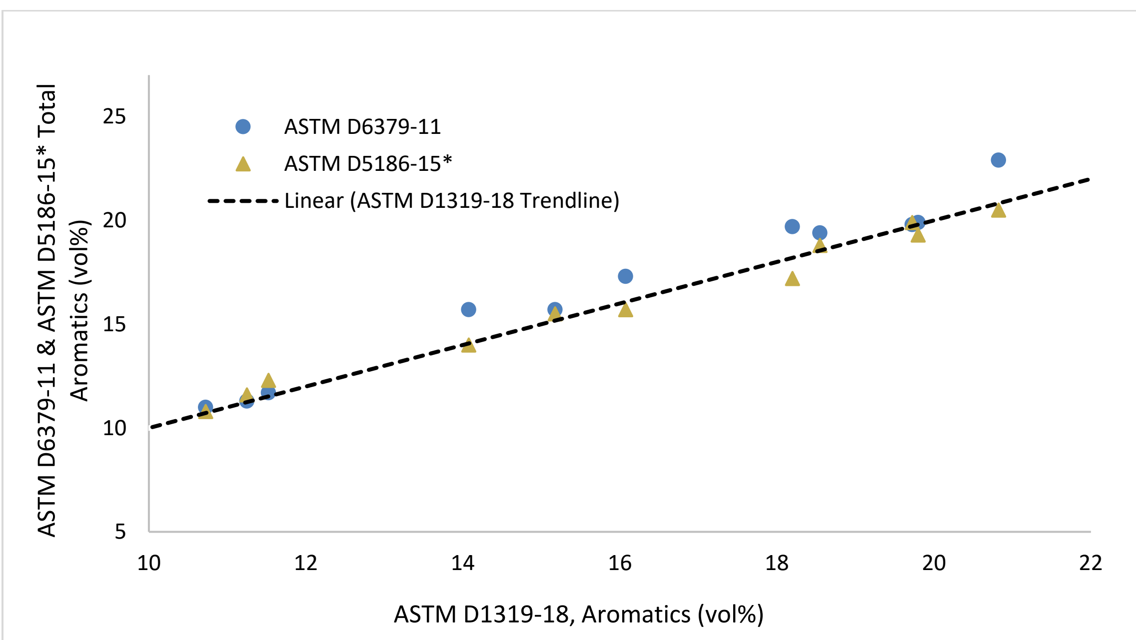


**Figure 2.** Total Aromatic Content Correlation (Close up)

Figure 2 highlights the data ≥10% aromatic content, where a majority of the sample data lies. By viewing this region it becomes easier to visualize the agreement between the aromatic content detected by each method.

## Supplemental Data

In addition to the currently approved methods in ASTM D1655, *Standard Specification for Aviation Turbine Fuels* [9], for measuring aromatic content there are two other approaches that have gained support in recent years; ASTM D8267-19, *Standard Test Method for Determination of Total Aromatic, Monoaromatic and Diaromatic Content of Aviation Turbine Fuels Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV)* [10], which has recently submitted a ballot for inclusion into ASTM D1655 and GC×GC-FID for bulk hydrocarbon distribution [11].

Table 9 compares the total aromatic content detected using ASTM D1319-18 and ASTM D8267-19. VUV Analytics requested the same 12 samples used in this study for testing via the D8267-19 method. The data in Table 1 was provided by VUV Analytics and represents a single test for each sample. ASTM D8267-19 proved to detect similar aromatic content to the results obtained from ASTM D1319-18 on these 12 fuels. However, more data is needed to conduct a thorough statistical analysis and determine if ASTM D8267-19 is equivalent to ASTM D1319-18 in aromatic detection capabilities.

**Table 9.** Total Aromatic Content Comparison of ASTM D1319-18 and ASTM D8267-19 (GC-VUV)

| | **Aromatic Content (% vol)** | | |
|---|---|---|---|
| **Sample** | **DOD 1 ASTM D1319-18** | **DOD 2 ASTM D1319-18** | **GC-VUV ASTM D8267-19** |
| 1 | 11.1 | 11.4 | 11.6 |
| 2 | 21.0 | 20.7 | 21.8 |
| 3 | 14.0 | 14.2 | 14.7 |
| 4 | 19.8 | 19.8 | 19.8 |
| 5 | 20.2 | 19.3 | 20.2 |
| 6 | 15.0 | 15.4 | 15.4 |
| 7 | 10.8 | 10.7 | 11.1 |
| 8 | 11.9 | 11.2 | 12.1 |
| 9 | 18.3 | 18.2 | 18.4 |
| 10 | 18.7 | 18.5 | 19.5 |
| 11 | 15.8 | 16.4 | 16.5 |
| 12 | 0.7 | 0.7 | 0.1 |

Table 10 shows GC×GC-FID data that is available for the study fuels. Although not cited in the fuel specifications, GC×GC has been used extensively by the DOD to characterize hydrocarbon fuels. GC×GC assesses all classes of hydrocarbons by carbon number, with the aromatics being classified as either alkyl benzenes, naphthalenes, or cycloaromatics (indans, tetralins, etc.). The sum of these is total aromatics and can be compared to D6379-11, D5186-15*, and D1319-18. GC×GC data is reported as vol%, which is convertible to mass% as the hydrocarbons are divided by carbon number and an average density for each type of hydrocarbon at each carbon number can be applied. The GC×GC data is shown in Table 10. The fuel density is also included in Table 10 for reference. The conversion data and equation from vol % to mass % for total aromatics is shown in Figure 3. This data originated in the DOD thermal stability survey. Since aromatics are denser than the other hydrocarbons in jet fuel, the mass% of aromatics is higher than vol %.

**Table 10.** Total Aromatic Content Comparison between ASTM D1319-18 & GC×GC-FID

| | **Aromatic Content (% vol)** | | | **Density** |
|---|---|---|---|---|
| **Sample** | **DOD 1 ASTM D1319-18** | **DOD 2 ASTM D1319-18** | **GC×GC-FID** | **kg/m$^3$** |
| 1 | 11.1 | 11.4 | 11.3 | 790 |
| 2 | 21.0 | 20.7 | 21.4 | 819 |
| 3 | 14.0 | 14.2 | 14.4 | 813 |
| 4 | 19.8 | 19.8 | 20.0 | 813 |
| 5 | 20.2 | 19.3 | 20.4 | 792 |
| 6 | 15.0 | 15.4 | 15.7 | 809 |
| 7 | 10.8 | 10.7 | 11.2 | 799 |
| 8 | 11.9 | 11.2 | 11.9 | 780 |
| 9 | 18.3 | 18.2 | 18.4 | 827 |
| 10 | 18.7 | 18.5 | 19.2 | 801 |
| 11 | 15.8 | 16.4 | 17.5 | 804 |
| 12 | 0.7 | 0.7 | 0.2 | 760 |

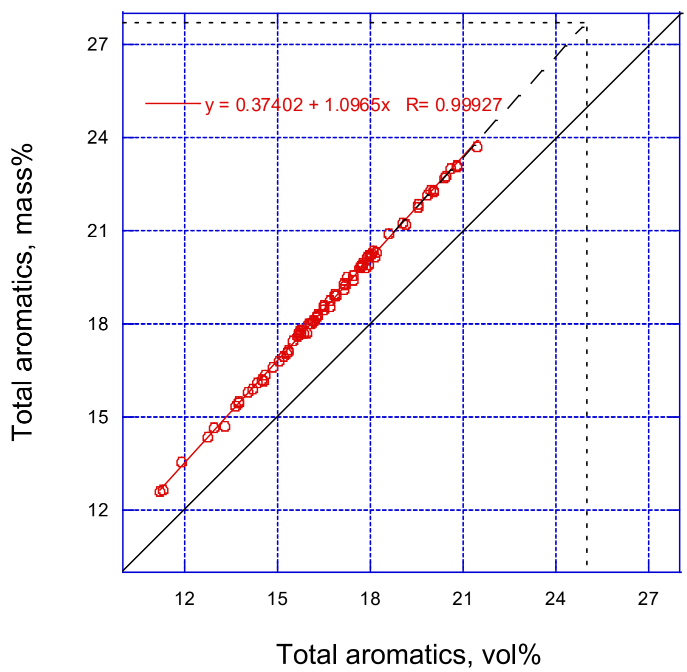


**Figure 3.** GC×GC-FID results for total aromatics from DOD survey showing conversion of vol % to mass %.

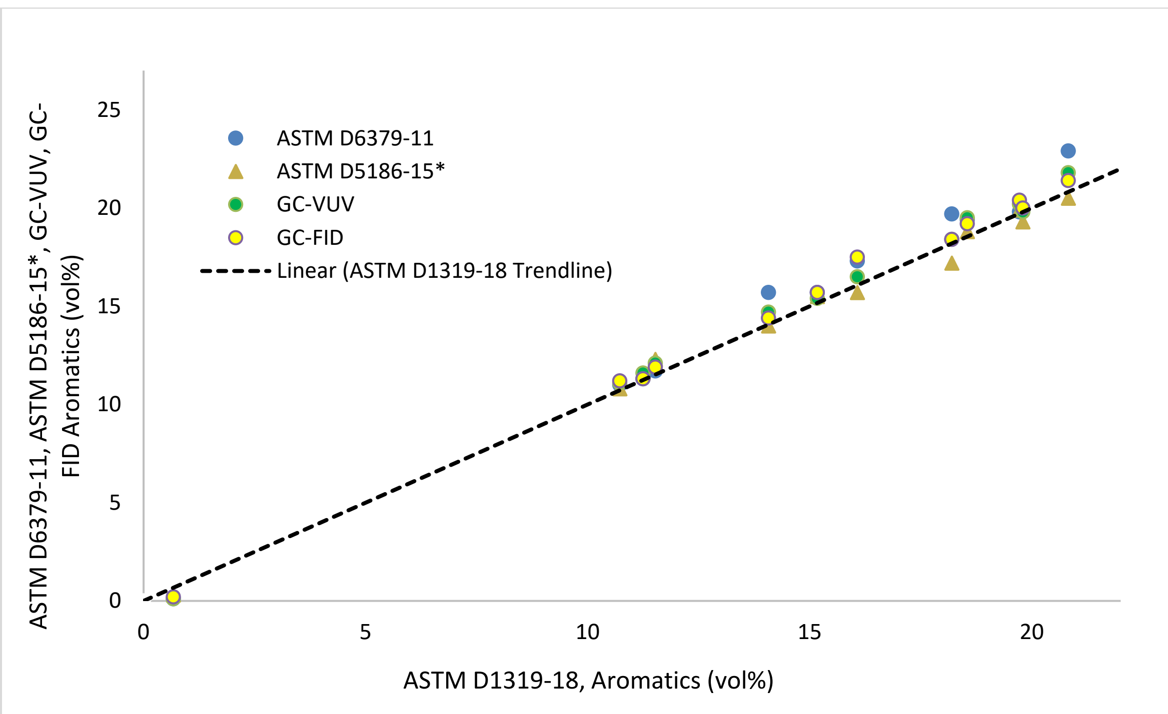


**Figure 4.** Aromatic Content Comparison by All Methods & Gas Chromatography

Gas chromatography data was plotted against D1319-18 data, and the trendline depicts the agreement among the data sets.

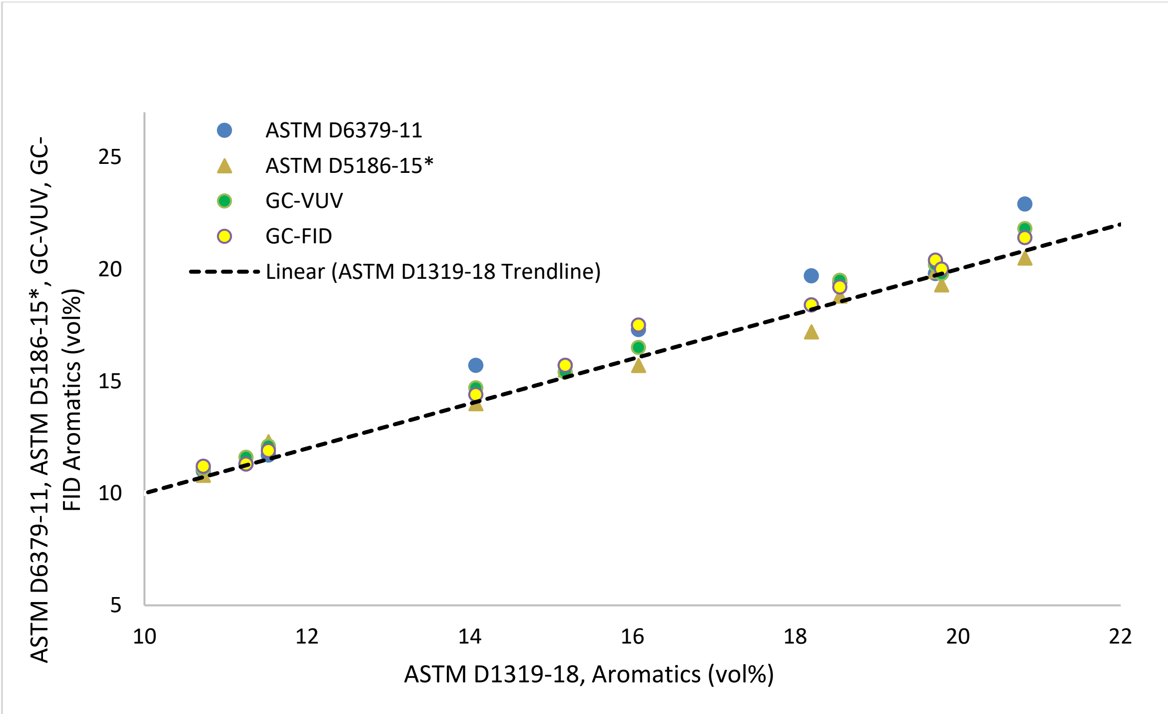


**Figure 5.** Aromatic Content Comparison by All Methods & Gas Chromatography (Close Up)

Figure 5 highlights the data ≥10% aromatic content, where a majority of the sample data lies. By viewing this region it becomes easier to visualize the agreement between the aromatic content detected by each method.

## 4. Conclusions and Recommendations

Statistical analysis has demonstrated good correlation between the total aromatic content detected by each method. Based on the results of this study the Tri-Service POL Users Group came to a consensus that there would be minimal risk to accepting ASTM D5186-15* and ASTM D6379-11 aromatic data if ASTM D1319-18 were to become unavailable.

Adopting ASTM D5186-15* or D6379-11 will pose different but theoretically simpler challenges to maintain testing accuracy. The FIA test conducted in ASTM D1319-18 is a more subjective assessment when compared to ASTM D5186-15* or D6379-11 as it is up to the user to determine where the hydrocarbon boundaries lie within the adsorption column to determine aromatic content. ASTM D5186-15* and D6379-11 both utilize more sophisticated instrumentation that calculates aromatic content digitally as opposed to manually. This eliminates the more prominent human error that exists in ASTM D1319-18. However, the tradeoff would be the increase in experience required for the user to run and maintain the more sophisticated instrument.

In addition, methods by means of gas chromatography have proven to be very reliable when calculating aromatic content in comparison to ASTM D1319-18. Figure 5 shows data points produced by GC-VUV and GC-FID are incredibly close to the ASTM D1319-18 trendline.

## References

[1] ASTM International, *ASTM D1319-18, Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption*, West Conshohocken: ASTM International, 2018.

[2] ASTM D6379-11(2019), *Standard Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection,* ASTM International, West Conshohocken, PA, 2019, www.astm.org

[3] ASTM D5186-20, *Standard Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels By Supercritical Fluid Chromatography*, ASTM International, West Conshohocken, PA, 2020, www.astm.org

[4] ASTM D8305-19, *Standard Test Method for The Determination of Total Aromatic Hydrocarbons and Total Polynuclear Aromatic Hydrocarbons in Aviation Turbine Fuels and other Kerosene Range Fuels by Supercritical Fluid Chromatography,* ASTM International, West Conshohocken, PA, 2019, www.astm.org

[5] K. Guyer, ASTM D1319 Fluorescent Indicator Dyed Gel Supply and Performance, Honeywell, 2019.

[6] K. Childress, *Evaluation of the Latest Batch of the Fluorescent Indicator Dyed Gel for Use with D1319 Analysis,* Southwest Research Institute, 2019.

[7] J. Bramer, A. Metz, A. Rymill, J. Schmitigal, P. Wrzesinski, *Evaluation of Prototype Dye to Measure Aromatic Content of Aviation Fuels Using ASTM D1319,* US ARMY CCDC Ground Vehicle System Center, 2020

[8] ASTM International, *ASTM E691-18, Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method,* West Conshohocken: ASTM - ASTM International, 2019.

[9] ASTM International, *ASTM D1655-19, Standard Specification for Aviation Turbine Fuels,* West Conshohocken: ASTM - ASTM International, 2019.

[10] ASTM D8267-19a, *Standard Test Method for Determination of Total Aromatic, Monoaromatic and Diaromatic Content of Aviation Turbine Fuels Using Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy Detection (GC-VUV), ASTM International*, West Conshohocken, PA, 2019, www.astm.org

[11] Johnson, K. J.; Loegel, T. N.; Metz, A. E.; Wrzesinski, P. J.; Shafer, L. M.; Striebich, R. C.; West, Z. Method for Detailed Hydrocarbon Analysis of Middle Distillate Fuels by Two-

Dimensional Gas Chromatography, version 1.3, Department of Defense Standard Operating Procedure, 2020.

## Appendix A - DOD Aromatics Round Robin Protocol

1. **Introduction**
   Recently, the dye used in ASTM D1319 experienced a formulation source change that has resulted in rejected dye lots and a shortage in functional product. Consequentially, ASTM proposed a ballot to include ASTM D5186 (SFC) as an alternative test method to ASTM D1319 in an effort to assist laboratories that no longer have access to functional dye lots. Since the December 2018 ASTM meeting, a decision was made to create a new Supercritical Fluid Chromatography test method specific for aviation fuel. The purpose of this Round Robin is for the DOD to evaluate the bias and equivalency between the ASTM aromatic methods for aviation fuel; D1319 (FIA), D6379 (HPLC), D5186 (SFC) independent of the ASTM ballot(s).

2. **Equipment**
   The following equipment, as specified in the below ASTM methods, shall be used in this Round Robin:
   - ASTM D1319-18 – Fluorescent Indicator Adsorption (FIA)
   - ASTM D6379-11 – High Performance Chromatograph (HPLC)
   - ASTM D5186-15 – Supercritical Fluid Chromatograph (SFC)*
     *Selerity Instruments model modified to run aviation fuel

Please see below table for laboratory capabilities:

Table I: DOD Laboratory Capabilities

| | **ASTM D1319 (FIA)** | **ASTM D6379 (HPLC)** | **ASTM D5186 (SFC)** |
|---|---|---|---|
| **DOD 2** | X | | X |
| **DOD 1** | X | X | |
| **DOD 3** | | X | |
| **DOD 5** | X | X | |
| **DOD 4** | | | X |

3. **Goals**
   The goals of this Round Robin are to:
   A. Evaluate the bias and equivalency between the ASTM Aromatic Methods for aviation fuel:
      1. D1319-18 (FIA)
      2. D6379-11 (HPLC)
      3. D5186-15 (SFC)

B. Present the data from this Round Robin at the ASTM D2 June meeting in Denver, CO.
    1. To accommodate this timeline, please submit completed data to Technical Coordinator (see information in Section 4) no later than 19 APR 2019.

**4. Test Methods and Procedure**

A. Accurately determine the aromatic, olefinic, and saturate content of aviation fuels in accordance with ASTM D1319-18, D6379-11, and ASTM D5186-15.

B. Procedure is as follows:
    1. AFRL will be sending the fuel samples to the selected laboratories
        a. 12 samples total that include F-24, JP-8, Jet A-1, JP-5, CHCJ-5, and HEFA.
    2. Three data worksheets will be provided for the Round Robin data. Please record the aromatic, olefinic, and saturate content of the fuels based the method you are performing.
        a. For example, DOD 1 shall perform ASTM D1319 and ASTM D5186 and record data on each respective data worksheets.
    3. Each laboratory shall run their specified test methods (see Table I) and fill out the data worksheets:
        a. ASTM D1319-18 shall be run in duplicate with the same technician
            - Please title and save the worksheet as “Service_Lab_ASTM D1319”.
        b. ASTM D6379-11 shall be run in duplicate with the same technician and the same instrument.
            - Please title and save the worksheet as “Service_Lab_ASTM D6379”.
            - If instrument provides data printouts, please save as a .pdf, “Service_Lab_ASTM D6379 Instrument Printout”.
        c. ASTM D5186-15 shall be run in duplicate with the same technician and the same instrument
            - Please title and save the worksheet as “Service_Lab_ASTM D5186.
            - If instrument provides data printouts, please save as a .pdf, “Service_Lab_ASTM D6379 Instrument Printout”.
    4. The completed data worksheets and instrument printout files shall be emailed to the Technical Coordinator:

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## Appendix B- Raw Data

**ASTM D1319 – FIA (Aromatics)**

| Sample (TRIPOL #) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **DOD 1** | 11.2 | 20.6 | 14.0 | 19.8 | 20.4 | 14.8 | 10.9 | 11.9 | 18.7 | 18.8 | 15.4 | 0.7 |
| | 11.6 | 21.3 | 14.0 | 19.8 | 20.0 | 15.2 | 10.7 | 11.9 | 17.8 | 18.5 | 16.1 | 0.7 |
| Mean | 11.4 | 21.0 | 14.0 | 19.8 | 20.2 | 15.0 | 10.8 | 11.9 | 18.3 | 18.7 | 15.8 | 0.7 |
| **DOD 2** | 11.4 | 20.5 | 14.2 | 19.1 | 19.3 | 15.4 | 10.7 | 11.0 | 17.9 | 18.3 | 16.4 | 0.7 |
| | 10.8 | 20.9 | 14.1 | 20.5 | 19.2 | 15.3 | 10.6 | 11.3 | 18.4 | 18.6 | 16.4 | 0.6 |
| Mean | 11.1 | 20.7 | 14.2 | 19.8 | 19.3 | 15.4 | 10.7 | 11.2 | 18.2 | 18.5 | 16.4 | 0.7 |

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**ASTM D1319 – FIA (Aromatics + Olefins)**

| Sample (TRIPOL #) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **DOD 2** | 13.8 | 22.4 | 16.4 | 21.4 | 21.3 | 17.7 | 13.5 | 13.0 | 20.4 | 20.4 | 18.4 | 1.6 |
| | 13.1 | 22.9 | 16.4 | 22.7 | 21.3 | 17.5 | 13.2 | 13.4 | 20.9 | 20.7 | 18.5 | 1.2 |
| Mean | 13.5 | 22.7 | 16.4 | 22.1 | 21.3 | 17.6 | 13.4 | 13.2 | 20.7 | 20.6 | 18.5 | 1.4 |
| **DOD 1** | 13.2 | 23.4 | 16.6 | 21.4 | 22.2 | 16.9 | 13.2 | 13.3 | 21.3 | 20.7 | 18.3 | 1.4 |
| | 12.8 | 22.7 | 15.9 | 20.9 | 21.7 | 17.1 | 12.8 | 13.6 | 20.0 | 20.2 | 18.5 | 1.4 |
| Mean | 13.0 | 23.1 | 16.3 | 21.2 | 22.0 | 17.0 | 13.0 | 13.5 | 20.7 | 20.5 | 18.4 | 1.4 |

**ASTM D8264-19 – Gas Chromatography - VUV**

| Sample (TRIPOL #) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mean | 11.6 | 21.8 | 14.7 | 19.8 | 20.2 | 15.4 | 11.1 | 12.1 | 18.4 | 19.5 | 16.5 | 0.1 |

**ASTM D5186 – SFC Total Aromatics**

| Sample (TRIPOL #) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **DOD 2** | 13.8 | 24.5 | 16.7 | 23.0 | 23.7 | 18.4 | 13.0 | 14.7 | 20.6 | 22.4 | 18.7 | 0.4 |
| | 13.8 | 24.5 | 16.7 | 23.1 | 23.7 | 18.4 | 12.9 | 14.6 | 20.5 | 22.3 | 18.7 | 0.3 |
| Mean | 13.8 | 24.5 | 16.7 | 23.1 | 23.7 | 18.4 | 13.0 | 14.7 | 20.6 | 22.4 | 18.7 | 0.4 |
| **DOD 4** | 13.8 | 24.1 | 16.5 | 22.6 | 23.3 | 18.3 | 12.7 | 14.3 | 20.2 | 22.1 | 18.5 | 0.5 |
| | 13.5 | 24.0 | 16.3 | 22.6 | 23.4 | 18.1 | 12.7 | 14.4 | 20.3 | 22.1 | 18.3 | 0.4 |
| Mean | 13.7 | 24.1 | 16.4 | 22.6 | 23.4 | 18.2 | 12.7 | 14.4 | 20.3 | 22.1 | 18.4 | 0.5 |

**ASTM D6379 – HPLC Total Aromatics**

| Sample (TRIPOL #) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **DOD 1** | 12.9 | 24.9 | 17.2 | 22.1 | 22.3 | 17.6 | 12.5 | 13.5 | 21.4 | 22.1 | 19.3 | 0.1 |
| | 12.5 | 24.9 | 17.0 | 22.1 | 22.3 | 17.5 | 12.4 | 13.5 | 21.3 | 21.9 | 19.3 | 0.1 |
| Mean | 12.7 | 24.9 | 17.1 | 22.1 | 22.3 | 17.6 | 12.5 | 13.5 | 21.4 | 22.0 | 19.3 | 0.1 |
| **DOD 3** | 12.5 | 24.1 | 16.5 | 21.3 | 21.9 | 16.7 | 11.7 | 13.1 | 20.6 | 20.8 | 18.1 | 0.1 |
| | 12.5 | 24.3 | 16.7 | 21.8 | 21.9 | 17.2 | 11.9 | 13.0 | 20.7 | 21.2 | 18.4 | 0.1 |
| Mean | 12.5 | 24.2 | 16.6 | 21.6 | 21.9 | 17.0 | 11.8 | 13.1 | 20.7 | 21.0 | 18.3 | 0.1 |

**Gas Chromatography - FID**

| Sample (TRIPOL #) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DOD 3 Mean | 11.3 | 21.4 | 14.4 | 20.0 | 20.4 | 15.7 | 11.2 | 11.9 | 18.4 | 19.2 | 17.5 | 0.2 |