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14. ABSTRACT

The fuel industry has relied on ASTM D1319 to quantify the aromatic content of aviation, diesel, and gasoline fuels. In 2018, Honeywell UOP changed the fluorescent indicator dye gel formulation in response to the olefin marker component no longer being available. The DOD conducted a testing program to determine if the prototype dye gel was suitable for testing aviation fuels. Diesel and gasoline fuels were excluded from this study as they are not primary fuels for the DOD. Honeywell UOP provided prototype dye gel from lot #3000000983 to US Army Combat Capabilities Development Command (CCDC) Ground Vehicle System Center (GVSC), Naval Air Systems Command (NAVAIR), and Air Force Petroleum Office (AFPET) laboratories. Twelve aviation (jet) fuel samples were tested in duplicate ranging in aromatic content from 0-24 percent volume. The Mean Delta across the samples, in all but one case, trends higher in measured aromatic content. Standard deviation indicates that the prototype dye gel is performing similarly to the legacy dye gel for jet fuel. The DOD concluded that the new prototype dye gel performs similarly to the legacy dye gel when testing aviation fuel.

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Evaluation of Prototype Dye to Measure Aromatic Content of Aviation Fuels Using ASTM D1319

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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
GVSC	Ground Vehicle Systems Center
HEFA	Hydroprocessed Esters and Fatty Acids
ILS	Interlaboratory Study
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
NFACT	Navy Fuel Analysis and Characterization Tool
R	Reproducibility
R^2	Coefficient of Determination
TRIPOL	Tri-Service Petroleum, Oil, and Lubricants
WPAFB	Wright-Patterson Air Force Base

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, 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. Users of the dye with the new component, specifically gasoline users, found the product to be different 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.

At the June 2019 ASTM meeting in Denver, Colorado, Honeywell UOP presented on a new formulation of the dye gel, showing that the new olefin marker was chemically similar to the discontinued olefin marker [2]. Honeywell UOP also indicated it was ready to begin selling the new lot of dye gel. During the same meeting, ASTM International Subcommittee D02.04.0C on Liquid Chromatography presented on the status of the Interlaboratory Study (ILS) planned to test the new dye gel [3]. Input from the attendees increased the scope and number of samples for the planned ILS. DOD representatives 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 for DOD purposes.

DOD representatives met with Honeywell UOP at the ASTM International meeting in June 2019 to request a teleconference to ask further questions and gain clarity on the new lot of dye. The teleconference was held on 10 July 2019, participants included representatives from the Air Force, Army, Navy, and DLA-Energy. Honeywell UOP was only able to share limited data to demonstrate the new (prototype) dye gel was chemically identical to the old (legacy) dye gel, as the formulation is proprietary. The DOD representatives requested samples of the prototype dye gel to initiate a DOD testing program to determine if the new formulation was acceptable for use in ASTM D1319-18. Honeywell UOP agreed to provide prototype dye gel to the Air Force, Army, and Navy laboratories for evaluation.

The DOD agreed to conduct a testing program to determine if the prototype dye gel was suitable for testing aviation (jet) fuels. Diesel and gasoline fuels were excluded from this study as they are not primary fuels for the DOD.

2. Approach

Test program

US Army Combat Capabilities Development Command (CCDC) Ground Vehicle System Center (GVSC), Naval Air Systems Command (NAVAIR), and Air Force Petroleum Office (AFPET) agreed to test the prototype dye gel. GVSC coordinated the testing program and collected and

analyzed the data for the study. As shown in Table 1, Air Force Research Laboratory (AFRL) distributed 12 jet fuel samples ranging in aromatic content from 0-24 volume percent to each laboratory. Honeywell UOP provided prototype dye gel from lot #3000000983 to each Service laboratory. 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 Part II - Prototype Dye Testing Information

DOD Laboratories	3
Samples	12 jet fuels; 0-24% aromatics: 4, F-24 3, JP-8 2, JP-5 1, Jet A-1 1, CHCJ-5 1, HEFA
Prototype Dye Gel Lot#	3000000983
Data Points (gathered in duplicate)	
ASTM D1319-18	36 (aromatics)

Each laboratory conducted testing using ASTM D1319-18 in duplicate (two columns per sample). The testing was conducted 19 July 2019 through 30 July 2019, and all data was submitted to GVSC by 1 August 2019.

Using the legacy dye, DOD laboratories also conducted ASTM D1319-18 testing 8 March 2019 through 24 April 2019 with the same 12 fuel samples provided by AFRL. For comparison, the aromatic data on the legacy dye gel will also be included in this report. Olefin data was recorded but is not included in this paper, as it was not the primary focus of this analysis due to not being in the specification requirement for aviation fuel.

3. Evaluation and Analysis

GVSC performed data analysis adhering to *ASTM E691-18, Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method* [4], this data can be found in Table 2. All legacy dye and prototype data values are in Appendix B.

From Table 2 it can be observed that the Mean Delta across the samples, in all but one case, trends higher in measured aromatic content. Standard deviation indicates that the prototype dye gel is performing similarly to the legacy dye gel for jet fuel.

Figure 1 graphs the mean aromatic content for the legacy dye gel (x-axis) versus the mean aromatic content for the prototype dye gel (y-axis). The solid line represents the legacy dye data values for the same fuel set. The R^2 value of 0.9976 is indicative of a linear correlation between the measured aromatic content of the prototype dye gel data against the legacy dye gel data. However, the data points of the prototype dye gel trend higher when compared to the corresponding legacy dye gel data points. Extrapolating out the trendline for the prototype dye gel to the aromatic content limit of 25 vol%, specified in ASTM D1655-19 [5] and MIL-DTL 83133K [6], the delta between prototype and legacy value increases by 1 vol%. The 1 vol% variation between the two dyes still falls within the published repeatability of 1.4% at 25 vol% found within ASTM D1319-18.

Table 2. ASTM D1319-18 Statistics: Aromatics

Sample (TRIPOL #)	**Mean** (Prototype)	**Mean** (Legacy)	**Mean Delta** (absolute)	**Standard Deviation** (Prototype)	**Standard Deviation** (Legacy)
Reporting to the Nearest 0.1vol%					
1	11.5	11.3	0.2	0.2	0.4
2	22.0	20.8	1.2	0.7	1.0
3	14.5	14.1	0.4	0.7	0.1
4	20.2	19.8	0.4	0.7	0.7
5	20.0	19.7	0.3	0.6	0.6
6	15.8	15.2	0.6	0.6	0.4
7	11.5	10.7	0.8	0.6	0.5
8	11.8	11.5	0.3	0.5	0.4
9	18.9	18.2	0.7	0.6	0.4
10	19.3	18.6	0.7	0.4	0.5
11	17.1	16.1	1.0	0.7	0.6
12	0.4	0.7	0.3	0.3	0.1

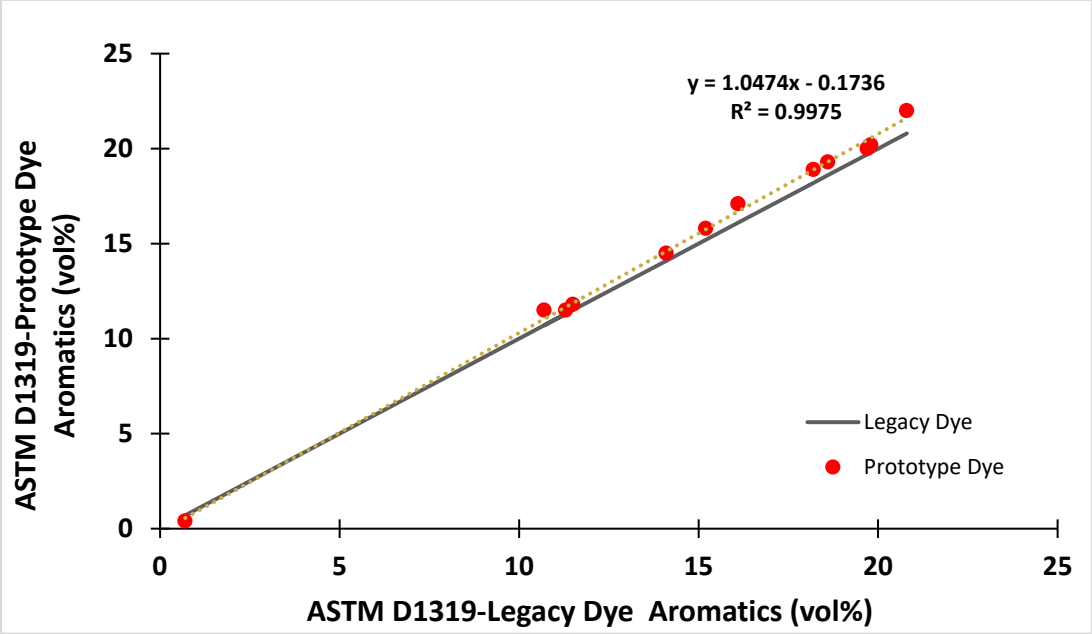

Figure 1. Comparison of Aromatic Content from Prototype Dye Data and Legacy Dye Data

4. Conclusions and recommendations

All DoD laboratories observed that olefin fluorescence of the prototype dye gel appeared dimmer, making it difficult to discern the aromatic and olefinic boundary during testing. This difficulty resulted in the observed 1 vol% increase in reported aromatic content. The use of the prototype dye gel presents an additional concern when testing aviation fuels procured that are near the 25 vol% maximum aromatic content limit specified within ASTM D1655-19 [5] and MIL-DTL 83133K [6], as it could lead to the prototype dye failing a fuel that previously would have passed with the legacy dye.

DOD procurement history collected from the Navy Fuel Analysis and Characterization Tool (NFACT) shows 5.70B US gallons of JP-5, JP-8, and F-24 were purchased from 2016 to 2018. During this period 0.9% of aviation fuels had an aromatic content above 24 vol% that would have been rejected due to high aromatic content if tested with the prototype dye. However, as previously stated within Section 3 of this report, the 1 vol% variation between the two dyes still falls within the published repeatability of 1.4% at 25 vol% found within ASTM D1319-18.

Taking into consideration the observations and the results of this study, in conjunction with the historical DOD fuel data provided by NFACT, allows the DOD to conclude that the new prototype dye gel performs similarly to the legacy dye gel when testing aviation fuel.

5. References

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

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

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

[4] 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.

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

[6] *MIL-DTL-83133K - TURBINE FUEL, AVIATION, KEROSENE TYPE, JP-8 (NATO F-34), NATO F-35, and JP-8+100 (NATO F-37),* Dayton: Air Force Petroleum Agency, 2018.

6. Appendix A

DOD Aromatics Round Robin – New Honeywell/UOP Dye

1. Introduction

Recently, the dye used in ASTM D1319-18 experienced a formulation source change that has resulted in rejected dye lots and a shortage in functional product, leaving laboratories unable to perform ASTM D1319-18. In response Honeywell UOP has created a new dye lot that is chemically similar to the legacy dye. The purpose of this Round Robin is for the DOD to evaluate if Honeywell's new dye lot is comparable in performance to functional legacy dyes.

2. Equipment

The following equipment, as specified in the below ASTM methods, shall be used in this Round Robin:

- ASTM D1319-18 – Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption

Please see below for participating laboratories:

Participating Laboratories
CCDC GVSC (Army)
NAVAIR (Navy)
AFPET (Air Force)

3. Goals

The goals of this Round Robin are to:

A. Perform ASTM D1319-18 using the prototype dye provided by Honeywell:
   - Lot Number: 3000000983

B. Present the data from this Round Robin at the August TRIPOL Face to Face Meeting at WPAFB
   - To accommodate this timeline, please submit completed data to Technical Coordinator (see information in Section 4) no later than 31 JULY 2019.

4. Test Methods and Procedure

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

B. Procedure is as follows:

1. Each laboratory shall reuse 12 fuel samples total that included F-24, JP-8, Jet A-1, JP-5, CHCJ-5, and HEFA that were sent by AFRL to participating laboratories in a previous DoD Aromatics Round Robin; samples identified as TRIPOL 1 through TRIPOL 12.
2. Each laboratory shall run ASTM D1319-18 and fill out the data worksheet provided:
    a. ASTM D1319-18 shall be run in duplicate, with the same technician, using the new dye lot provided by Honeywell UOP.
        - Please title and save the worksheet as "Service_Lab_ASTM D1319".
3. The completed data worksheets and instrument printout files shall be emailed to the Technical Coordinator:

    Bridget Dwornick
    bridget.l.dwornick.civ@mail.mil

7. Appendix B

Table 3. DoD Measured Aromatic Content Prototype Dye Data

Sample (TRIPOL #)	1	2	3	4	5	6	7	8	9	10	11	12
Lab A (vol%)	11.6	21.6	14.6	20.5	20.0	15.4	11.5	12.3	19.3	19.6	16.5	0.5
	11.6	22.4	14.5	20.3	20.5	15.3	11.5	11.6	19.1	20.0	17.4	0.4
$\bar{x}$	11.6	22.0	14.6	20.4	20.3	15.4	11.5	12.0	19.2	19.8	17.0	0.5
Lab B (vol%)	11.5	20.9	14.9	20.0	19.4	15.8	10.8	11.1	17.8	18.9	16.8	0.8
	11.1	21.5	14.6	19.9	19.8	15.9	10.8	11.6	18.8	19.1	17.0	0.5
$\bar{x}$	11.3	21.2	14.8	20.0	19.6	15.9	10.8	11.4	18.3	19.0	16.9	0.7
Lab C (vol%)	11.4	22.5	13.2	21.4	19.5	17.0	12.2	12.2	18.9	19.3	18.4	0.0
	11.6	22.8	15.1	19.3	20.8	15.6	12.2	12.0	19.3	19.1	16.6	0.0
$\bar{x}$	11.5	22.7	14.2	20.4	20.2	16.3	12.2	12.1	19.1	19.2	17.5	0.0

Table 4. DoD Measured Aromatic Content Legacy Dye Data

Sample (TRIPOL #)	1	2	3	4	5	6	7	8	9	10	11	12
Lab A (vol%)	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
$\bar{x}$	11.4	21.0	14.0	19.8	20.2	15.0	10.8	11.9	18.3	18.7	15.8	0.7
Lab B (vol%)	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
$\bar{x}$	11.1	20.7	14.2	19.8	19.3	15.4	10.7	11.2	18.2	18.5	16.4	0.7
Lab C* (vol%)	12.0	23.0	17.0	21.0	20.6	16.0	11.8	11.2	18.3	-	20.2	0.6
	-	-	-	-	-	-	-	-	-	-	-	-
$\bar{x}$	-	-	-	-	-	-	-	-	-	-	-	-

***Lab C unable to run in duplicate due to legacy dye shortage**