

FLASH POINT PERFORMANCE EVALUATION

**INTERIM REPORT
TFLRF No. 455**

**by
George R. Wilson, III
Principal Scientist**

**U.S. Army TARDEC Fuels and Lubricants Research Facility
Southwest Research Institute® (SwRI®)
San Antonio, TX**

**for
Jill Bramer
U.S. Army TARDEC
Force Projection Technologies
Warren, Michigan**

Contract No. W56HZV-09-C-0100 (WD23)

UNCLASSIFIED: Distribution Statement A. Approved for public release

March 2014

Disclaimers

Reference herein to any specific commercial company, product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the Department of the Army (DoA). The opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or the DoA, and shall not be used for advertising or product endorsement purposes.

Contracted Author

As the author(s) is(are) not a Government employee(s), this document was only reviewed for export controls, and improper Army association or emblem usage considerations. All other legal considerations are the responsibility of the author and his/her/their employer(s).

DTIC Availability Notice

Qualified requestors may obtain copies of this report from the Defense Technical Information Center, Attn: DTIC-OCC, 8725 John J. Kingman Road, Suite 0944, Fort Belvoir, Virginia 22060-6218.

Disposition Instructions

Destroy this report when no longer needed. Do not return it to the originator.

UNCLASSIFIED

FLASH POINT PERFORMANCE EVALUATION

INTERIM REPORT TFLRF No. 455

by
George R. Wilson, III
Principal Scientist

U.S. Army TARDEC Fuels and Lubricants Research Facility
Southwest Research Institute® (SwRI®)
San Antonio, TX

for
Jill Bramer
U.S. Army TARDEC
Force Projection Technologies
Warren, Michigan

Contract No. W56HZV-09-C-0100 (WD23)
SwRI® Project No. 08.14734.23.001

UNCLASSIFIED: Distribution Statement A. Approved for public release

March 2014

Approved by:



Gary B. Bessee, Director
U.S. Army TARDEC Fuels and Lubricants
Research Facility (SwRI®)

UNCLASSIFIED

UNCLASSIFIED

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 03-26-2014		2. REPORT TYPE Interim Report		3. DATES COVERED (From - To) December 2012-March 2014	
4. TITLE AND SUBTITLE FLASH POINT PERFORMANCE EVALUATION				5a. CONTRACT NUMBER W56HZV-09-C-0100	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Wilson, George				5d. PROJECT NUMBER SwRI 08.14734.23.001	
				5e. TASK NUMBER WD 23	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army TARDEC Fuels and Lubricants Research Facility (SwRI®) Southwest Research Institute® P.O. Drawer 28510 San Antonio, TX 78228-0510				8. PERFORMING ORGANIZATION REPORT NUMBER TFLRF No. 455	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army RDECOM U.S. Army TARDEC Force Projection Technologies Warren, MI 48397-5000				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT UNCLASSIFIED: Dist A Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT The primary question of this program was whether ASTM D6450 CCCFP is a suitable alternative to the military referee standard, ASTM D93 Pensky-Martens. The results generated in this program over a range of relevant samples, from TS1 to F76, show that ASTM D6450 provides a reliable answer when compared to ASTM D93. There is no indication of any performance enhancement from using ASTM D93 that would warrant the additional risk of an open ignition source in the PQAS-E.					
15. SUBJECT TERMS Flash point, fuels, PQAS-E, Army Mobile Laboratory, F76, RP2, TS1, JP8, JP5, JetA/A1, B20, ULSD					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	Unclassified		19b. TELEPHONE NUMBER (include area code)

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

UNCLASSIFIED

EXECUTIVE SUMMARY

The US Army uses a mobile laboratory system known as PQAS-E. This portable laboratory is contained in a standard ISO size shipping container. The system uses a closed environment with minimal ventilation. In the interest of safety several of the standard laboratory tests have been replaced with more portable, self-contained devices. Among those devices is the ASTM D6450 CCCFP Mini Flash Point tester.

The Mini Flash Point is not currently recognized in any of the fuel specifications, military or commercial, supported by the PQAS-E. Interservice discussions highlighted this issue. Due to the safety related nature of the flash point property, this program was commenced in an effort to provide substantiation of the suitability of using this Mini Flash Point unit in place of traditional ASTM D93 Pensky-Martens unit.

This program was not intended to be a formal precision program but rather a survey of the range of material that might be routinely tested by the PQAS-E system. In that pursuit fourteen samples, two commercial reference materials and twelve actual fuels, were assembled and tested for flash point. The fuels ranged from TS1 to F76. This represents a fairly wide range of distillate fuels but is a narrower scope than many of the research reports on the flash point methods.

The test program ran each sample in duplicate in each device tested. There were some operational issues with the Mini Flash loaned to TFLRF but those eventually were corrected and the program completed. The data shows a more than reasonable correlation between the ASTM D6450 Mini Flash and the military standard ASTM D93 Pensky-Martens Flash Point, with the worst case having a correlation coefficient, R , of 0.9570.

Based on the results of this program it seems very appropriate for the US Army to continue to use the Mini Flash system in the PQAS-E. The slight differences in results seen in this program do not support converting the analysis to open ignition method in tightly packed environment.

FOREWORD/ACKNOWLEDGMENTS

The U.S. Army TARDEC Fuel and Lubricants Research Facility (TFLRF) located at Southwest Research Institute (SwRI), San Antonio, Texas, performed this work during the period December 2012 through March 2014 under Contract No. W56HZV-09-C-0100. The U.S. Army Tank Automotive RD&E Center, Force Projection Technologies, Warren, Michigan administered the project. Mr. Eric Sattler (RDTA-SIE-ES-FPT) served as the TARDEC contracting officer's technical representative. Jill Bramer of TARDEC served as project technical monitor.

The authors would like to acknowledge the contribution of the TFLRF technical support staff.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
EXECUTIVE SUMMARY	ii
FOREWORD/ACKNOWLEDGMENTS.....	iii
LIST OF TABLES.....	v
LIST OF FIGURES	vi
ACRONYMS AND ABBREVIATIONS	vii
1.0 INTRODUCTION	1
2.0 FLASH POINT METHODOLOGY	1
2.1 ASTM D56 TAG CCFP	2
2.2 ASTM D93 PENSKEY-MARTENS CCFP	2
2.3 ASTM D3828 SMALL SCALE CCFP	2
2.4 ASTM D6450 CONTINUOUSLY CLOSED CUP FLASH POINT (CCCFP, “MINI FLASH”).....	2
2.5 ASTM D7094 MODIFIED CONTINUOUS CLOSED CUP FLASH POINT (MCCCFP, “MINI FLASH”)	3
2.6 FLASH POINT IS A RELATIVE VALUE.....	3
3.0 TEST SAMPLES	4
3.1 CL12-3453 & 3475	4
3.2 CL12-3491	5
3.3 CL13-4811&4812	5
3.4 CL13-4837&4838	5
3.5 CL13-4969	5
3.6 CL13-5094,5095&5486	5
3.7 CL13-5670,5671&5672	6
4.0 TEST PROGRAM	6
5.0 TEST RESULTS.....	8
6.0 CONCLUSION.....	12
7.0 RECOMMENDATIONS.....	14
8.0 REFERNCES	14

LIST OF TABLES

<u>Table</u>	<u>Page</u>
Table 1. Test Samples for WD 23.....	4
Table 2. Test Results.....	8
Table 3. Sample Information with Average Results from This Program	12

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
Figure 1. Flash Point Results Compared to D93.....	9
Figure 2. ASTM D6450 Compared to D93	11

ACRONYMS AND ABBREVIATIONS

Acronym	Definition
ASTM	ASTM International, consensus standards and specifications
B20	Biodiesel containing 20% FAME
CCCFP	Continuous Closed Cup Flash Point
CCFP	Closed Cup Flash Point
CIS	Commonwealth of Independent States, former Soviet block
COA	Certificate of Analysis
CONUS	Continental United States
F76	High flash marine diesel fuel, US Navy
ILCP	Inter Laboratory Crosscheck Program
IP	formerly Institute of Petroleum, now used only as test designation.
ISO	International Organization for Standardization
Jet A/A1	Standard flash jet fuel, commercial
JP5	High flash jet fuel, US Navy
JP8	Standard flash jet fuel, US Military
MCCCFP	Modified Continuous Closed Cup Flash Point
NAWC	Naval Air Warfare Center
NEG	National Exchange Group
PM	Pensky-Martens
PQAS-E	Petroleum Quality Analysis System - Enhanced, US Army's mobile laboratory
R	Correlation Coefficient
R ²	Coefficient of Determination
RP2	Kerosene rocket fuel
SD	Standard Deviation
TFLRF	TARDEC Fuels and Lubricants Research Facility (SwRI)
TS1	Low flash jet fuel from CIS suppliers to DLA-Energy
ULSD	Ultra Low Sulfur Diesel

1.0 INTRODUCTION

The US Army is using ASTM D6450 [1] Continuously Closed Cup Flash Point (CCCFP) analysis. Recently, the use of CCCFP has been criticized as an inappropriate method since MIL-DTL-83133H [2] only allows the following flash point test methods: ASTM D56 [3], D93 [4], D3828 [5], or JP 170 [6] (with D93 as the referee method). The rejoinder is that these open flame/ignition systems are inappropriate for a closed environment like the Petroleum Quality Analysis System-Enhanced (PQAS-E). Regardless, there is interest in establishing the similarities and differences of the CCCFP method in comparison to the approved methods.

In addition to the above concern there are additional points of interest. Currently there is a plan to convert CONUS jet fuel acquisitions from JP-8 to Jet A [7]. Jet A flash point is controlled by ASTM D56, a method known to vary from D93 in results. Also, there is an alternative method, ASTM D7094 [8] and an alternative supplier available for the equipment that runs the CCCFP and these will also be evaluated.

To evaluate the efficacy of the various test methods the US Army TARDEC Fuels and Lubricants Research Facility – SwRI (TFLRF) assembled fourteen samples, a mixture of commercial standards and actual fuels. These samples were tested in duplicate using each of the methods of interest.

2.0 FLASH POINT METHODOLOGY

All of the flash point methods used in this program are a variation of closed cup methodology (CCFP). A sample (volume varying by method) is placed in a sealed cup and heated. At intervals stated in the methods, an ignition source is introduced into the ullage space above the sample. When the hydrocarbon vapor and the oxygen content is sufficient the vapor will ignite, thus signifying the flash point. The methods tested follow.

2.1 ASTM D56 TAG CCFP

This is the oldest of the CCFP methods in current use. It is the referee method for commercial jet fuel. In this method the sample in the closed cup is heated by transferring heat through a water bath. This gives the ASTM D56 Tag method the practical range of just above 0 °C to approximately 100 °C. (The IP 170 Abel Flash Point is similar in nature but was not tested in this program.) DLA-Energy [9] routinely acquires TS1 [10] from CIS [11] countries for use in Afghanistan. TS1 has a minimum flash point of 27 °C (though the 2012 average [12] was 38.6 °C) so, for traditional CCFP devices, the ASTM D56 is better scoped to support that fuel type. For this program TFLRF used an ISL [13] automatic model.

2.2 ASTM D93 PENSKEY-MARTENS CCFP

In this method the closed cup is heated directly by the heat source. It is actually scoped for samples ranging from 40 °C to 360 °C, therefore the minimum flash point of 38 °C for low flash jet fuels, military and commercial, is technically out of scope. However this method has been used successfully for decades with great success although there might be some concern with TS1 samples approaching their specification limits. For this program TFLRF used a Herzog [14] automatic model.

2.3 ASTM D3828 SMALL SCALE CCFP

This method uses a small sample (2 ml) placed in a directly heated aluminum block. This method is often called the “Setaflash” for both the name of the original manufacturer[15] and the primary use where the unit is set at the specification limit and the fuel is simply evaluated in a GO/NOGO fashion. The method can also be used to find an actual flash point value. This is a relatively slow test and is conducted manually. For this program TFLRF used a model with a gas flame.

2.4 ASTM D6450 CONTINUOUSLY CLOSED CUP FLASH POINT (CCCFP, “MINI FLASH”)

In this variant of the closed cup flash point test, a small sample (1 ml) is placed in a cup that is inserted into the test device. Instead of a periodic opening where a ignition source is introduced,

the CCCFP includes an ignition source in the sealed chamber. The system uses an arc source (similar to a spark plug) and periodically creates a spark until ignition is detected by a pressure wave. By keeping the system sealed the ignition is completely contained, a desirable feature for a portable device where an open flame or ignition might be a problem. For this program TFLRF used instruments from Grabner [16] and Eralytics [17]. This provides additional information on the main goal, evaluating ASTM D6450 in relation to the standard methods, and offers an evaluation of a competitive unit that can result in reduced cost for maintaining the PQAS-E system.

2.5 ASTM D7094 MODIFIED CONTINUOUS CLOSED CUP FLASH POINT (MCCCFP, “MINI FLASH”)

This method uses the same basic hardware as used in ASTM D6450 except the sample size is increased to 2 ml. The posit is that the increased sample size gives improved precision across the range of materials and expected flash points being tested. While the PQAS-E program has standardized on ASTM D6450, there is an interest in knowing if the newer method would provide better data. Switching between methods is supposed to be simple a matter of switching the sample cup. For this program TFLRF used the same instruments from Grabner and Eralytics for both ASTM D6450 and D7094 testing.

2.6 FLASH POINT IS A RELATIVE VALUE

The concept of “flash point” is simple: At what temperature is there sufficient flammable material in the vapor phase to sustain an ignition? The problem is that it is not a fundamental property but one contingent on the system conditions in which it is evaluated. The closed cup system has established itself for nearly a century [18] of acceptable evaluation of anticipated flash points. The important evaluation of novel closed cup devices is if it produces results comparable to the established methods.

3.0 TEST SAMPLES

When flash point manufacturers evaluate systems, their challenge is to ensure the system provides reliable results across the range of materials that may be tested. For use in the PQAS-E system, the important performance characteristic is that it gives reliable results with the samples routinely run. In this case a variety of fuels and fuel components were evaluated. The sample list is shown in Table 1 below.

Table 1. Test Samples for WD 23

Sample #	Material		FP	D56		D93		D3828	
			Literature	Average	SD	Average	SD	Average	SD
CL12-3453	HRJ-1 CAF-7815					44.86	1.21		
CL12-3475	B20-1 from WD17					59.13	1.60		
CL12-3491	AF-8114 RP-2					67.78	COA		
CL13-4811	F76 - Marine Diesel Fuel								
CL13-4812	JP5 - High Flash Jet Fuel								
CL13-4837	Cannon Low Refence		46	50	Est.	55	Est.		
CL13-4838	Cannon High Reference		62	66	Est.	72	Est.		
CL13-4969	TS1 - Low Flash Jet Fuel								
CL13-5094	ASTM ILCP JF1207			45.87	1.06			46.09	1.86
CL13-5095	ASTM ILCP JF1211			44.06	1.39			44.33	1.30
CL13-5486	ASTM ILCP JF1303			43.10	1.43			43.41	1.00
CL13-5670	ASTM ILCP DF21302					62.25	1.48	60.35	5.64
CL13-5671	ASTM NEG Diesel No. D1076					60.10	1.39		
CL13-5672	ASTM NEG Diesel No. D1075					32.10	4.78		

Table 1 above lists the fourteen samples acquired for this program in order of the TFLRF sample number. Also included is the available flash point information for these samples. This data is not specifically intended for evaluating the results generated in this program but rather it is compiled for general reference. A general discussion of sample origins follows:

3.1 CL12-3453 & 3475

These samples came from the US Army sponsored, TFLRF fuel storage program. The HRJ-1 is a sample of HEFA SPK [10] that is used to blend semi-synthetic jet fuel. The B20-1 is a sample of a 20% biodiesel blend [20]. The US Army acquires significant amounts of B20 for domestic use, so the ability to evaluate this material is relevant to system performance

3.2 CL12-3491

RP-2 [21] is the low sulfur version of the kerosene type rocket fuel that is currently being purchased by DLA-Energy. The flash point listed in Table 1 above comes from the provided Certificate of Analysis (COA).

3.3 CL13-4811&4812

These samples were provided by NAWC [22]. F76 [23] and JP5 [24] are the standard high flash fuels used by the US Navy and US Marine expeditionary forces. The US Army has provided PQAS-E systems to US Marines so it is important that it work well with their preferred fuels.

3.4 CL13-4837&4838

These are commercially available reference standards [25]. The table includes reported literature values for equilibrium flash point and the estimated ASTM D56 and D93 flash point values. The standard reference materials for the CCCFP are anisole and dodecane. The anisole has a CCCFP flash point, 43 °C, in the range of interest but it is an aromatic material that has a strong smell. The dodecane has a CCCFP flash point, 79 °C, well beyond the expected range. These commercial reference standards are n-decane and undecane, respectively. As paraffins they are relatively odor free and more compatible with the closed PQAS-E environment.

3.5 CL13-4969

TS1 is the low flash, 27 °C minimum, jet fuel originally developed by the Soviet Union for use in very cold climates. The US Military has been using significant amounts of TS1 in Afghanistan and support bases in CIS countries.

3.6 CL13-5094,5095&5486

These samples are from the ASTM ILCP, Inter Laboratory Crosscheck Program, jet fuel program. ASTM sends out samples three times a year for laboratories to run the standard specification tests, submit the data to ASTM and then compare performance to the cumulative

test results. Since it is in support of the ASTM D1655 and D7566 specifications, it calls for ASTM D56 and D3828.

3.7 CL13-5670,5671&5672

These are ASTM diesel fuel program samples. CL13-5670 is from the diesel fuel ILCP program. The diesel ILCP calls for ASTM methods D93 and D3828 for flash point. Samples CL13-5671&5672 are from the ASTM NEG, the National Exchange Group, program for comparing results on cetane engines and derived cetane number test equipment. The former program runs all the ASTM D975 specification properties. The latter program collects that ASTM D975 specification data which is volunteered.

4.0 TEST PROGRAM

With the initial samples in hand, the test program commenced. Each sample was to be tested in duplicate on each available device, one each for ASTM D56, D93 and D3828 and two each for ASTM D6450 and D7094. In the course of running the program there were performance issues with the Grabner CCCFP/MCCCFP device.

The first group of tests included the TS1 sample (see Table 1) and the Grabner instrument stood out in its inability to get a reasonable number for the flash point. A discussion with the technician running the testing revealed the instrument was taking extraordinary effort to achieve results. An effort to resolve the problems with the instrument led to the discovery that the test sample thermocouple was incorrectly placed.

Following instructions from the manufacturer, TFLRF relocated the thermocouple location, and that appeared to solve the problem. The program was restarted with the complete set of samples. While the TS1 sample got reasonable results, there were still problems with the rest of the samples. An attempt to run the samples again resulted in the system failing.

The manufacturer determined that the unit was still in the extended warranty period that was part of the PQAS-E program and repaired and recalibrated it at no expense to the project. Upon return it functioned adequately and the requisite retests were run without a notable operational problem.

All of the instruments were operated in accordance with the appropriate ASTM method and the manufacturer's instructions. Running the manual ASTM D3828 test reinforced the value of the modern automatic units. Among the automatic units the CCCFP/MCCCFP units were clearly more suited for use in a small, mobile lab. It is not just the lack of an open flame that makes the more traditional units problematic, it is also the hardware that is complex in nature and requires careful assembly, disassembly and cleaning. The CCCFP/MCCCFP units have a simple cartridge borne sample cup that is inserted and removed from the instrument easily and takes a minimal amount of effort to clean.

Between the Grabner and the Eralytics the latter was clearly the preferred, at TFLRF, for implementation. The controls were more logically laid out and the instrument required less operator interaction to get a successful run (even after the Grabner repair). Grabner has a revised instrument that have similar improvements to the user interface.

5.0 TEST RESULTS

The results for the testing are compiled in Table 2 below:

Table 2. Test Results

Sample #	D 93 Pensky-Martens	D 56 TAG	D 6450 Eralytics	D 7094 Eralytics	D 6450 Grabner	D 7094 Grabner	D3828B Seta Flash
CL12-3453	42.5	43.8	43.8	47.7	44.3	47.3	42.0
	42.5	43.8	43.8	47.7	45.3	47.2	42.0
CL12-3475	58.5	61.7	58.7	59.7	61.3	63.2	58.0
	59.5	61.7	59.7	59.7	60.3	63.2	58.0
CL12-3491	62.5	61.7	61.8	63.7	63.3	65.1	61.0
	62.5	61.7	62.8	63.7	63.3	65.1	61.0
CL13-4811	72.0	70.6	73.5	72.5	73.3	76.2	72.2
	71.0	70.6	74.5	72.5	73.3	76.2	72.2
CL13-4812	63.0	63.9	62.5	63.4	63.3	66.2	63.9
	63.0	63.8	62.5	63.4	63.2	66.3	63.9
CL13-4837	51.0	50.3	48.5	50.4	49.0	51.3	50.6
	50.0	51.1	48.5	50.4	49.0	51.3	50.6
CL13-4838	66.0	63.0	63.5	64.4	64.0	68.3	63.3
	65.5	63.0	63.5	64.4	64.1	68.3	63.3
CL13-4969	36.0	35.8	37.5	36.4	37.0	37.3	35.0
	36.0	35.8	37.5	36.5	36.0	37.3	35.0
CL13-5094	45.5	47.7	47.8	47.7	47.1	65.3	45.0
	45.5	47.9	47.8	47.7	47.1	65.4	45.0
CL13-5095	44.0	42.8	44.5	45.5	45.2	46.5	40.6
	44.0	42.3	44.5	45.5	45.2	46.5	40.6
CL13-5486	42.5	47.7	44.8	47.7	45.2	60.5	43.0
	42.0	47.7	45.8	47.7	46.2	59.5	44.0
CL13-5670	59.5	61.8	61.8	60.7	63.4	63.3	61.0
	59.5	61.8	61.8	60.7	63.5	63.3	61.0
CL13-5671	56.5	61.7	59.8	58.7	61.5	78.4	59.0
	56.5	61.7	60.8	59.7	61.5	78.4	59.0
CL13-5672	43.5	58.7	42.8	48.7	54.5	60.5	47.7
	43.5	58.7	42.8	47.8	54.5	60.5	47.0

After the issues surrounding getting a reliable number for TS1, it was satisfying to see the results appear to be reasonably grouped (data in red box in Table 2). Obtaining this result would identify this fuel as comparatively high in volatility with the requisite handling care needed. The lower the flash point, the more important that the unit get a reliable number.

Since a primary goal was to evaluate how CCCFP/MCCCFP units compared to ASTM D93, the next step in the analysis was to compare the results of the those devices to ASTM D93. See Figure 1.

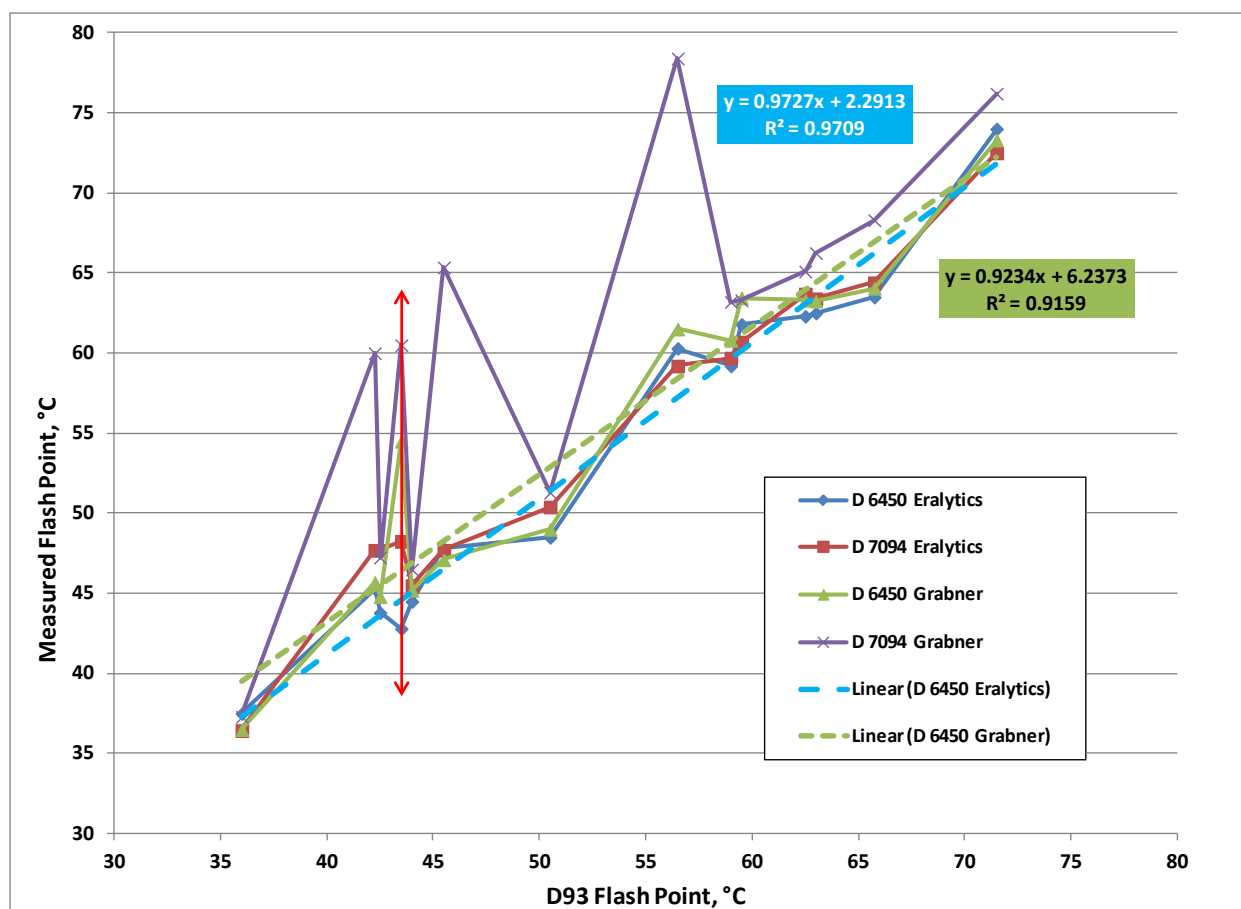


Figure 1. Flash Point Results Compared to D93

The plot in Figure 1 assumes that the ASTM D93 value is the correct value and illustrates the variation therefrom. *Note: the lines connecting the data points are for emphasis and do not represent a relationship.* Comparing the ASTM D6450 data to the D93, by manufacturer, shows the Grabner instrument has a correlation coefficient [26], R , of 0.9570 and the Eralytics instrument has a correlation coefficient, R , of 0.9853. By this analysis, ASTM D6450 clearly describes the same system as does ASTM D93.

In this data there are two items of concern:

- 1) The large excursions from the average for some of the Grabner ASTM D7094 tests
- 2) The scatter for the sample marked by the double arrow red line-

Even with these issues to discuss, the initial review shows that the ASTM D6450 results give excellent correlation to ASTM D93.

Since the project was coming to an end, there was no ability to invest additional time or money in trying to determine why the Grabner instrument was having trouble with ASTM D7094 while performing well with ASTM D6450. All that can be done now is to speculate on the cause. The Grabner unit used by TFLRF is part of the PQAS-E inventory of instruments and has only been used for ASTM D6450 in its service life. The sample cups for ASTM D6450 and D7094 are supposed to be interchangeable but there are subtle differences. Perhaps the instrument in question has taken a set fit to the cups used in the ASTM D6450 method and the ASTM D7094 cup does not work consistently. This would have to be considered before contemplating a change from method in current use.

The sample marked by the red line is CL13-5672, one of the two NEG samples tested. In Table 1 the results of the exchange group evaluation of flash point are highlighted in red because they are well below the specification requirement, 52 °C minimum, for #2 ULSD [27]. A closer look at the NEG data showed that low average was from testing with a bimodal distribution with peaks around 29 °C and 38 °C. The sample was clearly contaminated. While the sample apparently weathered away some of the contamination before being acquired by TFLRF, the trailing effects can be seen in the scattered data.

The primary intent of this program was to evaluate the use of ASTM D6450 in place of D93 with typical fuel samples. Therefore the data was re-analyzed comparing only these methods and eliminating the contaminated sample. This comparison is illustrated in Figure 2.

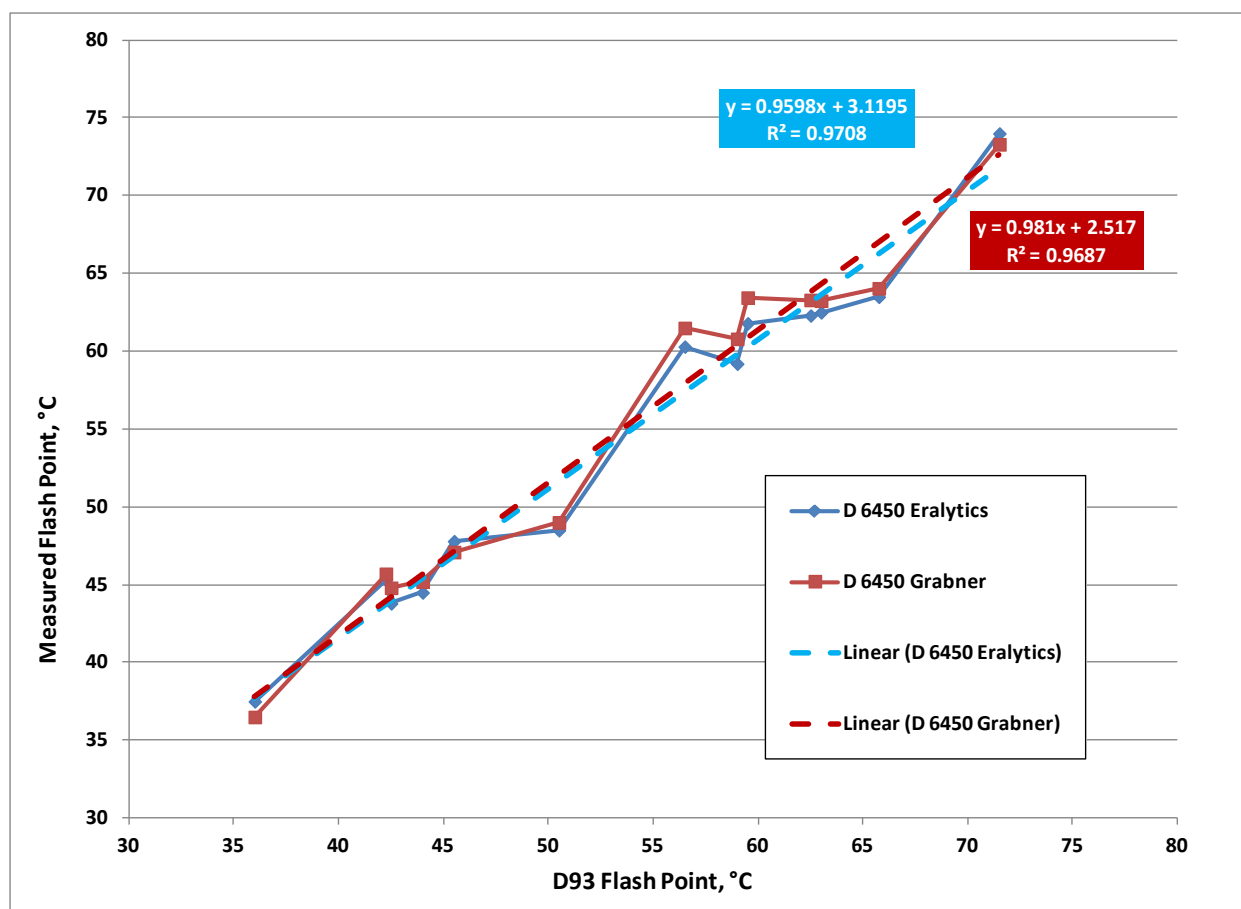


Figure 2. ASTM D6450 Compared to D93

The data in Figure 2 clearly illustrates an excellent relationship between these methods. The correlation coefficients, R , for this analysis are 0.9853 for the Eralytics, 0.9842 for the Grabner and 0.9843 cumulative. For a 1% level of significance (1 chance out of 100 the correlation is random), the required R value [28] for thirteen samples is only 0.641. This data shows the excellent correlation between methods.

These comparisons were done on average values. The repeatability of the methods was excellent. The average difference between repeats was 0.1 °C and the maximum difference between repeats was 1.0 °C. The primary differences were driven by the methods used. While it was not the intent to evaluate the data based on known or estimated results for the samples, it is instructive to compare them. Following in Table 3 below, the information from Table 1 has been appended to

include the average results from fuels tested in this program, without the Grabner data for ASTM D7094 and the known contaminated sample.

Table 3. Sample Information with Average Results from This Program

			FP	D56		D93		D3828		Average	
Sample #	Material		Literature	Average	SD	Average	SD	Average	SD	Average	SD
CL12-3453	HRJ-1 CAF-7815					44.86	1.21			44.10	1.95
CL12-3475	B20-1 from WD17					59.13	1.60			59.73	1.32
CL12-3491	AF-8114 RP-2					67.78	COA			62.42	0.97
CL13-4811	F76 - Marine Diesel Fuel									72.35	1.20
CL13-4812	JP5 - High Flash Jet Fuel									63.32	0.51
CL13-4837	Cannon Low Reference	46		50	Est.	55	Est.			49.95	0.94
CL13-4838	Cannon High Reference	62		66	Est.	72	Est.			64.00	0.96
CL13-4969	TS1 - Low Flash Jet Fuel									36.21	0.82
CL13-5094	ASTM ILCP JF1207			45.87	1.06			46.09	1.86	46.82	1.19
CL13-5095	ASTM ILCP JF1211			44.06	1.39			44.33	1.30	43.73	1.77
CL13-5486	ASTM ILCP JF1303			43.10	1.43			43.41	1.00	45.36	2.13
CL13-5670	ASTM ILCP DF21302					62.25	1.48	60.35	5.64	61.38	1.26
CL13-5671	ASTM NEG Diesel No. D1076					60.10	1.39			59.70	1.86

The average standard deviation (SD) for the samples in this program is 1.30, which roughly equivalent [29] to a Reproducibility of 3.64 °C. For samples ranging in flash point from 36° to 72 °C, the Reproducibility of ASTM D93, the military reference test, would vary from 2.6° to 5.1 °C. The standard deviations for the methods used in the program also compare favorably with the data reported for the discrete methods used on the supplied samples.

6.0 CONCLUSION

The primary question of this program was whether ASTM D6450 CCCFP is a suitable alternative to the military referee standard, ASTM D93 Pensky-Martens. The results generated in this program over a range of relevant samples, from TS1 to F76, show that ASTM D6450 provides a reliable answer when compared to ASTM D93. There is no indication of any performance enhancement from using ASTM D93 that would warrant the additional risk of an open ignition source in the PQAS-E.

Two secondary questions were also posed:

- 1) Should the US Army consider changing to the ASTM D7094 MCCCCFP method?
- 2) Is the Eralytics instrument a suitable alternative to the Grabner instrument?

Based on the unusual behavior of the Grabner instrument when running the ASTM D7094 test, it is not possible to make a recommendation, one way or the other. Without further testing and evaluation, probably best left to the manufacturer, it is not possible to determine whether this issue was limited to this machine or if it represents a problem for units that have been in extended long term use running the ASTM D6450 method. The Eralytics unit ran the ASTM D7094 method without a problem but the correlation was essentially the same as with the ASTM D6450 method so that does not suggest a benefit from changing.

The Eralytics instrument performed both the ASTM D6450 and D7094 testing without incident. The improved user interface made it the preferred method in testing at TFLRF. There should be no issue with using the Eralytics instrument in future PQAS-E installations.

Finally, part of the program was to evaluate the samples using ASTM D56 Tag CCFP. This is the referee method for commercial Jet A/A1 produced in accordance with ASTM D1655. This is important to the US Army because DLA-Energy is converting to commercial Jet A/A1 in CONUS. Historically, ASTM D56 was thought to routinely produce flash points significantly lower than those generated in ASTM D93 (as seen in the estimated flash points for the reference standards quoted in Table 1). This program does not support such a conclusion. There has not been a significant cross comparison program between these two methods since the automated methods have become the de facto standard. Since ASTM has added ASTM D93 to the commercial jet fuel specification, ASTM D1655, it would be helpful if the ASTM ILCP for jet fuel started collecting data for a comparison (and for ASTM D6450 and D7094).

7.0 RECOMMENDATIONS

Based on the results of this program, TFLRF offers the following recommendations:

- 1) Use this report to confirm the appropriateness of using the ASTM D6450 method in place of ASTM D93 for evaluating flash points of the fuels routinely tested in PQAS-E. The differences between one instrument running ASTM D93 and the two instruments running ASTM D6450 were within a range that would be considered normal for the differences between three ASTM D93 instruments.
- 2) Recommend the addition of ASTM D6450 to the next revision of MIL-DTL-83133 and to the next revision of ASTM Specifications D1655 and D7566. (The data generated on the Eralytics instrument supports the same recommendation for ASTM D7094.)
- 3) Hold off on any plan to convert to ASTM D7094 until the problems associated with the Grabner instrument used in this study are properly evaluated.
 - a. Review this information with the manufacturer
 - b. Consider testing additional units from the PQAS-E program for efficacy when running ASTM D7094
- 4) Include the Eralytics instrument on the list of instruments suitable for use in PQAS-E. Having an alternative supplier makes logistics and acquisitions easier to manage.
- 5) Recommend to the ASTM ILCP group that their Jet Fuel Cross Check program add methods D93, D6450 and D7094 to the list of tests to be analyzed.

8.0 REFERENCES

1. Standard Test Method for Flash Point by Continuously Closed Cup (CCCFP) Tester, ASTM International, W. Conshohocken, PA
2. JP-8 Specification, maintained by US Air Force
3. Standard Test Method for Flash Point by Tag Closed Cup Tester, ASTM International, W. Conshohocken, PA

4. Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester, ASTM International, W. Conshohocken, PA
5. Standard Test Methods for Flash Point by Small Scale Closed Cup Tester, ASTM International, W. Conshohocken, PA
6. Abel Flash Point Method, Energy Institute, UK
7. ASTM D1655 Standard Specification for Aviation Turbine Fuels, ASTM International, W. Conshohocken, PA
8. Standard Test Method for Flash Point by Modified Continuously Closed Cup (MCCCFP) Tester, ASTM International, W. Conshohocken, PA
9. The Defense Logistics Agency (DLA) department that acquires all of the fuel for the US military.
10. Low flash point jet fuel prepared in accordance with GOST 10227
11. Commonwealth of Independent States, countries formerly part of Soviet block
12. From 2012 PQIS Annual Report, DLA-Energy, Ft. Belvoir, VA
13. ISL is division of Petroleum Analyzers Company (PAC) Houston, TX
14. Herzog is division of PAC
15. Stanhope-Seta, London, UK
16. Grabner Instruments is a division of Ametek, Berwyn, PA
17. Vienna, Austria
18. ASTM D56 originally published in 1918
19. As defined by Annex A2 of ASTM D7566 the Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons, ASTM International, W. Conshohocken, PA
20. As defined by ASTM D7467 the Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20), ASTM International, W. Conshohocken, PA
21. MIL-DTL-25576E the Detail Specification Propellant, Rocket Grade Kerosene, maintained by the US Air Force
22. Naval Air Warfare Center, Pawtuxent Naval Air Station
23. MIL-DTL-16884L the Detail Specification Fuel, Naval Distillate, maintained by the US Navy
24. MIL-DTL-5624U the Detail Specification Turbine Fuel, Aviation, Grades JP-4 and JP-5, maintained by the US Navy
25. Cannon Instruments, State College, PA
26. The correlation coefficient, R, is often confused with the coefficient of determination, R², which is reported in MS Excel chart regressions.

27. Table 1 of ASTM D975 Standard Specification for Diesel Fuel Oils, ASTM International, W. Conshohocken, PA
28. Probability, Statistics and Random Processes, Louis Maisel, Simon and Schuster, pg 276, New York, 1971
29. According to ASTM E177 the Standard Practice for Use of the Terms Precision and Bias in ASTM Test Methods, (ASTM International, W. Conshohocken, PA), “The reproducibility limit is 2.8 times the reproducibility standard deviation.” This calculation is often used to estimate precision based on test data such as those produced in this program.