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EVALUATION OF ASTM D5006 FOR ACCURACY, REPEATABILITY, AND REPRODUCIBILITY FOR FUEL SYSTEM ICING INHIBITOR (FSII) CONCENTRATIONS < 0.10% BY VOLUME AND VARYING FUEL COMPOSITION

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14. ABSTRACT
Evaluation of ASTM D5006-11 for quantitation of fuel system icing inhibitor (FSII) concentrations < 0.10% by volume in aviation fuel was performed to provide guidance regarding potential measurement accuracy at low concentrations. This evaluation is necessary due to recent reductions in the JP-8 FSII procurement and use limits. The study was comprised of two phases: Evaluation of control standards of 0.010 to 0.080% in a specification Jet A-1 fuel, and effect of fuel type (primarily aromatic content) for target concentrations of 0.040 and 0.070%. Measurements of blind samples were performed by two different operators/laboratories, using all currently approved refractometers. Primary findings include: (1) Excellent repeatability (< ±3%) and interlaboratory reproducibility (< ±5%), (2) Overestimation of FSII concentration by 2-10% for 'non-typical' aviation fuels, (3) Slight differences in measured values with different approved refractometers, (4) Analog refractometers require user-estimation to three decimals, and (5) Fuel composition can affect FSII extraction percentage into aqueous phase. Overall, the D5006 repeatability and reproducibility appears to be substantially better than reported in the current method. Further evaluation via round-robin laboratory testing may be required for improved statistical analysis.

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1. Executive Summary

Evaluation of the accuracy, repeatability and reproducibility of ASTM D5006-11 for quantitation of Fuel System Icing Inhibitor (FSII) concentrations < 0.10% by volume in aviation fuel was performed to provide guidance regarding potential measurement accuracy at low concentrations. The study was comprised of two phases:

- Evaluation of control standards with DiEGME concentrations ranging from 0.010-0.080% by volume using a clay-treated Jet A-1 fuel.
- Evaluation of the effect of fuel type (primarily aromatic concentration) on the D5006 measurement for two target control concentrations (~0.040 and ~0.070%).

During the study, control solutions were prepared and separated into multiple blind samples for evaluation of both method repeatability and reproducibility. Measurements were performed by two different operators/laboratories, using all currently approved refractometers. Primary findings from the study include:

- Repeatability for a given operator/laboratory was excellent; typically < ±3% of the relative concentration.
- Reproducibility between laboratories was excellent; typically < ±5% of the relative concentration.
- The analyses typically overestimated the true FSII concentration by 2-10% for 'non-typical' aviation fuels.
- Small differences in the measured values were observed for quantitation with the different approved refractometers.
- Use of Analog refractometers requires estimation of measured FSII concentration to three decimals via operator interpretation.
- Fuel composition affected the percentage of FSII extracted into the aqueous phase during analysis. For a specific fuel, negligible change in the extraction efficiency was observed with varying FSII concentration for the range of concentrations evaluated.

Overall, this evaluation demonstrated that the repeatability and reproducibility of D5006 at low FSII concentrations appears to be substantially better than the values reported in the current method. Further evaluation of the accuracy of D5006 at reduced FSII levels via round-robin laboratory testing may be required to provide sufficient data for improved statistical analysis.

2. Background

The United States Air Force (USAF) mandates the use of Di-Ethylene Glycol Monomethyl Ether (DiEGME) as a Fuel System Icing Inhibitor (FSII) additive in JP-8. The USAF reduced the use and procurement limits of the FSII additive required in JP-8 military fuel in Fall, 2012. The minimum use limit has been reduced to 0.04% by volume (per T.O. 42B-1-1) while the fuel specification (MIL-DTL-83133H with AMENDMENT 1) requires that JP-8 is procured with between 0.07-0.10% by volume. A potential issue during implementation of FSII concentrations ≤ 0.10% by volume is the quantitation accuracy of the currently approved test method, ASTM D5006-11. The method currently states that the repeatability and reproducibility of the test method are 0.005-0.009% and 0.018-0.021%, respectively (as determined in ASTM Research Report:D02-1251). However, the interlaboratory round robin used to determine these was performed using blind samples of either 0.08 or 0.12% in various types of fuels. The current study was performed in two phases to provide additional preliminary guidance regarding the accuracy, repeatability and reproducibility of ASTM D5006 for quantitation of FSII concentration at lower levels. The first phase evaluated several control standards ranging from 0.010-0.080% by volume in a typical specification Jet A-1 fuel. The second phase investigated the potential effect of fuel type on the quantitation for two control concentrations (~0.040 and ~0.070%). The primary fuel property varied was the total aromatic content. Measurements were made by two different operators in the Air Force Research Laboratory (AFRL) and Air Force Petroleum Agency (AFPA) fuels laboratories at Wright Patterson Air Force Base (WPAFB). All approved refractometers were used during the measurements made in this study. In addition, the FSII concentration in the control samples was measured using Gas Chromatography/Mass Spectrometry (GC/MS) in Selected Ion Monitoring (SIM) mode.

3. Experimental Testing Methodology

3.1 FSII Concentration from 0.010-0.080% in Jet A-1 Fuel

Eight control standards with DiEGME concentrations ranging from 0.010-0.080% were prepared volumetrically with clay treated Jet A-1 (< 15 ppmV residual DiEGME; termed POSF 5237). Sufficient total volume was prepared for each standard to be divided into 5 separate blind samples, randomly numbered 1-40. Three of each control solution (3 x 8 standards = 24 total samples) were analyzed for total DiEGME concentration by ASTM D5006 by a single operator at AFRL, two of each remaining concentration were analyzed by a single operator at AFPET (16 samples).

AFRL Analysis Notes (Phase 1):

- The ASTM D5006 method was followed for FSII quantitation.
- Measurements were performed under similar lab conditions over a three-day period. Samples 1-8 were analyzed Day 1, 9-16 on Day 2 and 17-24 on Day 3.
- For each control standard analysis, three separate measurements were performed and averaged (using the same aliquot) using the following refractometers:
    - Gammon HB/2D Digital
    - MISCO JPX-DIEGME Digital
    - Gammon SC HB B/2
    - Reichart Brix 35 HP
    - Reichart AR 200 Digital (report refractive index only)
- Refractometer calibration was verified between each set of two samples using water. All refractometers showed zero drift except the Gammon HB/2D, which occasionally required re-zeroing.
- The reported data include:
    - Digital Refractometers
        - Average Refractive Index (RI)
        - FSII concentration to three decimal places
    - Analog Refractometers
        - FSII concentration to three decimal places by user interpolation
- FSII concentration in the pre-extracted fuel was quantified using GC/MS in SIM-mode.
    - Performed for verification of control concentration
    - Three separate control standards were prepared (0.037, 0.054, and 0.120%) and analyzed via D5006; post-extracted fuel samples were analyzed for residual FSII concentration

AFPET Analysis Notes (Phase 1):

- The ASTM D5006 method was followed for FSII quantitation.
- Measurements performed only using Gammon SC HB B/2

- FSII concentrations were reported to two decimal places only (one significant figure at < 0.10% by volume)

3.2 Effect of Fuel Type on D5006 Measurement

Control standards with target DiEGME concentrations of approximately 0.040 and 0.070% were prepared in three different aviation fuels. The primary fuel property of interest for variation was the total aromatic content. The results from this testing were compared to those obtained during the expanded concentration evaluation with Jet A-1. The aromatic concentration and general description for all fuels evaluated in this study are shown in Table 1.

Table 1. Description of Fuels used for Method Evaluation.

Fuel POSF ID	Fuel Type	Aromatic Content (%)	Density (g/mL)	Description
5018	Synthetic Paraffinic Kerosene	0	0.755	SPK derived from Natural Gas via FT Synthesis (Syntroleum). Comprised of *n* - and *iso* -paraffins. Mildly branched; used for B-52 Alternative Fuel Certification
7696	SPK/Jet A-1 Blend*	9.1	0.776	50/50 Blend by volume of 5018 and 5237
5237	Jet A-1	19.2	0.797	Low Sulfur Jet A-1
3602	Jet A	24.0	0.820	High Aromatic Jet A
*Blend properties determined via averaging of neat fuels				

Sufficient total volume was prepared for each standard to be divided into 5 separate blind samples, randomly numbered 41-70. Three of each control solution (3 x 6 standards = 18 total samples) were analyzed for total DiEGME concentration by ASTM D5006 by a single operator at AFRL, two of each remaining concentration were analyzed by a single operator at AFPET (12 samples).

AFRL Analysis Notes (Phase 2):

- The ASTM D5006 method was followed for FSII quantitation.
- Measurements were performed under similar lab conditions over a 3-day period.
- For each control standard analysis, three separate measurements were performed and averaged (using the same aliquot) using the following refractometers:
    - Gammon HB/2D Digital
    - MISCO JPX-DIEGME Digital
    - Gammon SC HB B/2
    - Reichart Brix 35 HP
    - Reichart AR 200 Digital (report refractive index only)

- Refractometer calibration was verified between each set of two samples using water. All refractometers showed zero drift except the Gammon HB/2D, which occasionally required re-zeroing.
- The reported data include:
  - Digital Refractometers
    - Average Refractive Index (RI)
    - FSII concentration to three decimal places
  - Analog Refractometers
    - FSII concentration to three decimal places by user interpolation

- FSII concentration in the pre-extracted fuel was measured using GC/MS in SIM-mode.
  - Performed for verification of control concentration
  - All post-extracted fuel samples were analyzed for residual FSII concentration

AFPET Analysis Notes (Phase 2):

- The ASTM D5006 method was followed for FSII quantitation.
- Measurements performed using all refractometers as used by AFRL.
  - Measurements reported/estimated to three decimal places
- All post-extracted fuel samples were analyzed for residual FSII concentration.

4 Results and Discussion

4.1 FSII Concentration from 0.010-0.080% in Jet A-1 Fuel

The data collected during the investigation of ASTM D5006-11 accuracy for concentrations from 0.010-0.080% in Jet A-1 (POSF 5237) are shown in Table 2. There was generally good consistency and repeatability between the measured samples and the control concentration for each refractometer and the GC/MS analysis. The Gammon HB/2D Digital refractometer had the highest variability, which was most likely affected by multiple re-zeroing during the study. It was found there was bias between the measured FSII concentration using the Gammon and MISCO digital refractometers. These differences are likely due to the scale basis chosen independently by MISCO and Gammon, which is the mathematical relationship between refractive index and DiEGME concentration. The Gammon uses the same relationship between refractive index and percent DiEGME as used in the original B/2 refractometer, while the MISCO instrument is based on the Brix calculation in D5006. The AFPA analyses were in reasonable agreement with the control concentrations; these samples will not be discussed further since they were only reported to two decimal places for this phase of the study.

The calculated average concentration values, standard deviation (68% confidence), and percent difference between the measured values and the control concentration (determined from volumetric preparation) for each refractometer are shown in Table 3. Figure 1 shows a comparison of the percent difference for the average concentration values as a function of the control concentration and refractometer used. As shown, there was excellent agreement in accuracy (typically < ±5% relative difference) for all measurements performed. Only the Gammon HB/2D Digital unit showed a higher variance, which is most likely due to the aforementioned re-zeroing. Agreement of < ±5% at a FSII concentration of 0.040% results in a variance of ~0.002% FSII, which is an encouraging result for quantitation at low concentrations. However, further investigation of the method accuracy, possibly including a round robin evaluation, would be required to provide adequate data for a robust statistical analysis.

The residual concentration of FSII in the Jet A-1 following water extraction was quantified using GC/MS for three additized test samples to provide guidance regarding the extent of FSII extraction with the current test method for a 'typical' aviation fuel. These test samples were prepared with 0.037, 0.054, and 0.120% FSII by volume and analyzed via D5006. As shown in Table 4, approximately 90-91% of the FSII was consistently extracted from this Jet A-1 fuel by the water over a wide range of initial FSII concentrations in the fuel. Determination of the resulting DiEGME concentration in the extracted aqueous phase was performed via mass balance calculation, showing that the aqueous phase concentration can approach 7-8% for high FSII fuel concentrations for the current fuel/water ratios used in the method. This information may be beneficial if it is subsequently determined that the D5006 method should be modified to improve accuracy and precision at lower FSII concentrations. For example, knowledge of the extent of FSII extraction for varying fuel/water volumes and the resulting aqueous phase concentration (with refractive index values) could assist with determining the optimal extraction ratios and refractive index ranges for quantitation (Falkiner, 1983).

It is important to note that recording of the FSII concentration to three decimal places (two significant figures at concentrations < 0.10% by volume) is crucial to obtain the excellent accuracy and repeatability observed in this evaluation. For the analog reading refractometers, this involves user estimation of the third decimal place .

Table 2: Results from Testing with Jet A-1 (POSF 5237).

% FSII Based on Volumetric Preparation	Sample	AR200	Gammon HB 2/D		Misco		Gammon HB B/2	Brix 35HP		GC/MS	AFPET (Gammon HB B/2)
		nD	*nD*	*DiEGME*	*nD*	*DiEGME*	*DiEGME*	*Reading*	*DiEGME*	*DiEGME*	*DiEGME*
0.012	7	**1.33370**	1.33400	0.013	1.33399	0.013	0.013	0.6	0.012	0.012	
	16	**1.33400**	1.33380	0.011	1.33389	0.012	0.011	0.6	0.012		
	23	**1.33360**	1.33400	0.013	1.33391	0.012	0.012	0.6	0.012		
	29										0.01
	35										0.01
0.023	3	**1.33450**	1.33480	0.025	1.33484	0.024	0.025	1.1	0.022	0.022	
	11	**1.33460**	1.33480	0.026	1.33494	0.026	0.023	1.1	0.022		
	18	**1.33440**	1.33483	0.025	1.33451	0.022	0.023	1.1	0.022		
	27										0.02
	34										0.02
0.029	9	**1.33490**	1.33540	0.033	1.33519	0.029	0.031	1.5	0.03	0.028	
	14	**1.33490**	1.33537	0.033	1.33519	0.029	0.031	1.5	0.03		
	17	**1.33480**	1.33540	0.033	1.33502	0.027	0.030	1.5	0.03		
	31										0.03
	40										0.03
0.035	19	**1.33527**	1.33570	0.038	1.33565	0.035	0.037	1.8	0.036	0.033	
	21	**1.33510**	1.33530	0.032	1.33542	0.032	0.032	1.6	0.032		
	24	**1.33510**	1.33570	0.038	1.33550	0.034	0.035	1.8	0.036		
	28										0.02
	39										0.03
0.044	2	**1.33600**	1.33640	0.048	1.33622	0.043	0.049	2.3	0.046	0.042	
	5	**1.33600**	1.33600	0.041	1.33625	0.044	0.042	2.1	0.042		
	20	**1.33580**	1.33640	0.048	1.33619	0.043	0.043	2.1	0.042		
	30										0.03
	33										0.03
0.056	4	**1.33680**	1.33730	0.062	1.33711	0.056	0.060	2.9	0.058	0.057	
	8	**1.33660**	1.33680	0.053	1.33705	0.055	0.059	2.8	0.056		
	22	**1.33670**	1.33730	0.061	1.33712	0.056	0.059	2.9	0.058		
	32										0.05
	38										0.05
0.067	1	**1.33750**	1.33810	0.073	1.33791	0.068	0.070	3.4	0.068	0.067	
	10	**1.33757**	1.33820	0.074	1.33793	0.069	0.070	3.4	0.068		
	15	**1.33730**	1.33800	0.071	1.33783	0.067	0.067	3.3	0.066		
	26										0.06
	37										0.06
0.078	6	**1.33820**	1.33880	0.083	1.33864	0.079	0.080	3.9	0.078	0.075	
	12	**1.33790**	1.33890	0.084	1.33838	0.075	0.073	3.6	0.072		
	13	**1.33800**	1.33833	0.076	1.33862	0.079	0.080	3.9	0.078		
	25										0.08
	36										0.07

Table 3: Comparison of Average, Standard Deviation, and Percent Difference from the Control for the Measured FSII Concentration as a Function of Refractometer and Control Concentration.

Control Volume (%)	Gammon HB/2D			MISCO			Gammon HB B/2			Brix 35 HP		
	Average	StDev	% Diff	Average	StDev	% Diff	Average	StDev	% Diff	Average	StDev	% Diff
0.012	0.012	0.001	2.8%	0.012	0.001	2.8%	0.012	0.001	0.00%	0.012	0.000	0.0%
0.023	0.025	0.001	10.1%	0.024	0.002	4.3%	0.024	0.001	2.9%	0.022	0.000	-4.3%
0.029	0.033	0.000	13.8%	0.028	0.001	-2.3%	0.031	0.001	5.7%	0.030	0.000	3.4%
0.035	0.036	0.003	2.9%	0.034	0.002	-3.8%	0.035	0.003	-1.0%	0.035	0.002	-1.0%
0.044	0.046	0.004	3.8%	0.043	0.001	-1.5%	0.045	0.004	1.5%	0.043	0.002	-1.5%
0.056	0.059	0.005	4.8%	0.056	0.001	-0.6%	0.059	0.001	6.0%	0.057	0.001	2.4%
0.067	0.073	0.002	8.5%	0.068	0.001	1.5%	0.069	0.002	3.0%	0.067	0.001	0.5%
0.078	0.081	0.004	3.8%	0.078	0.002	-0.4%	0.078	0.004	-0.4%	0.076	0.003	-2.6%

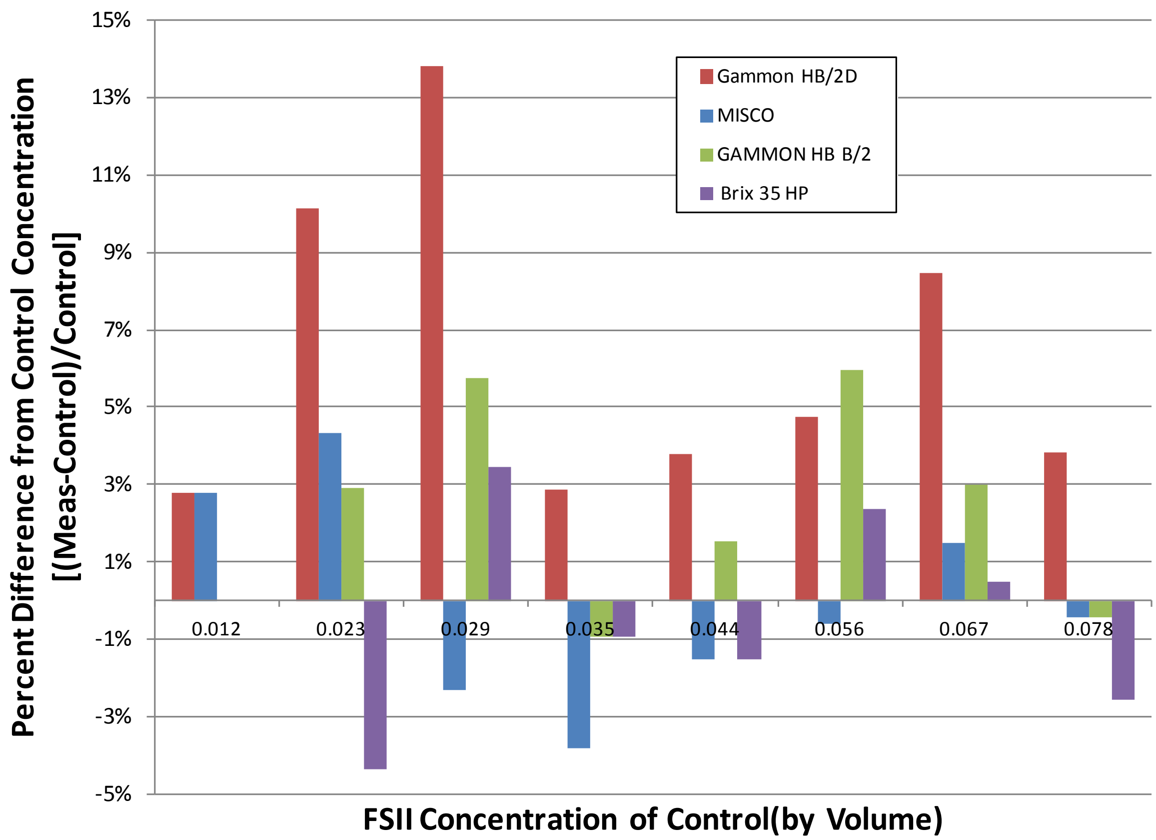

Figure 1: Comparison of Relative Percent Difference between Measured Average FSII Concentration as a Function of Refractometer Type and Control Concentration.

Table 4: Comparison of Measured FSII Concentration in Fuel Pre- and Post-Water Extraction. The Percent DIEGME Extracted by Water and Resulting Concentration in the Aqueous Phase were Calculated via Mass Balance.

GC/MS Analysis		Calculated	
Vol % FSII in Fuel Pre-Extraction	Vol % FSII in Fuel Post-Extraction	Vol % DiEGME Extract to Water	Vol % DiEGME in Aqueous Phase
0.037	0.0035	91	2.6
0.054	0.0055	90	3.7
0.120	0.0120	90	8.0

4.2 Effect of Fuel Type on D5006 Measurement

The accuracy and repeatability of D5006 at DiEGME concentrations < 0.10% by volume in a Jet A-1 fuel was shown to be excellent. During the initial development of D5006 for measurement of Ethylene Glycol Monomethyl Ether (EGME) in aviation fuel, it was reported that the fuel aromatic content can potentially affect the water extraction efficiency, and resulting quantitation, of the method (see ASTM RR:D02-1251). It was reported that increasing aromatic content in aviation turbine fuel increased the extraction percentage. In this study, measurements were performed to investigate the potential effect of fuel composition on the method repeatability and reproducibility. Evaluation was performed using the fuels shown in Table 1, which span the range from zero aromatic concentration for the Synthetic Paraffinic Kerosene (SPK) fuel produced via Fischer-Tropsch synthesis (POSF 5018), to a petroleum-derived Jet A (POSF 3602) with a total aromatic content (24.0%) near the maximum specification limit (25.0%). Testing was performed with each fuel using control concentrations near 0.040 and 0.070% DiEGME by volume. In addition, a 50% blend by volume of the SPK and Jet A-1 used in the previous phase of this study was also evaluated (9.1% aromatic content, termed POSF 7696). Measurements were performed by both AFRL and AFPA using all approved refractometers.

The measured concentrations, calculated repeatability and reproducibility, and standard deviations (68% confidence) for fuels 5018, 7696 and 3602 are shown in Tables 5-7. In addition, the percentage of FSII extracted, as determined via GC/MS quantitation and mass balance calculation, are reported for each sample. The repeatability for each laboratory was excellent, typically < ±0.001% for the measurements performed. The reproducibility was slightly higher (typically < ±0.003%), but once again substantially better than reported in the method. A comparison of the overall average values with each refractometer for the fuels and concentrations evaluated is shown in Figure 2 and Table 8. In general, there was less than a 7% difference between the control concentration and measurements, except for the Gammons HB/2D refractometer, which also showed the largest variance during the preceding multi-concentration evaluation with Jet A-1 (POSF 5237). The differences between the control and quantified FSII concentrations are larger than shown in Figure 1 for the aforementioned testing; it should be reiterated that the previous comparison is only a measure of repeatability as inter-laboratory comparison was not possible. Review of the data indicates that there may possibly be a slight bias to the measurements, as almost all average measurements were higher than the control concentrations. However, the cause for this potential bias is currently unknown. There was no distinct trend observed for the FSII quantitation with respect to fuel composition/type. The accuracy was best at the moderate to typical aromatic concentrations (POSF 7696 and 5237), but was worse at the low (POSF 5018) and high (POSF 3602) aromatic concentrations.

The percentage of FSII extracted during the analyses was determined by quantitation of the residual FSII in the fuel after water extraction and closure of the mass balance. A distinct and reproducible trend in the percentage of FSII extracted to the aqueous phase was observed for the various fuels, as shown in Table 8. The residual FSII was not quantified in the specific Jet A-1 (POSF 5237) samples shown, but this fuel had ~90-91% FSII extracted over the range of concentrations studied (see Table 4). Consistency in the extraction percentages for a given fuel was excellent both within and between the two laboratories in this study. It appears that an increase in aromatic concentration (or a comparable fuel property) reduced the extraction efficiency of FSII into the aqueous phase. Since the D5006 determines the FSII concentration in the fuel via refractive index measurement of the water extract and corresponding calibration curve, a significant change in the extraction percentage could potentially affect the accuracy of the measurement. Since the refractometer correlations were developed using typical petroleum-derived kerosene jet fuels, an increase in the FSII extraction percentage would result in a bias to higher measured values. Preliminary calculations were performed to estimate the effect of this potential bias; using an extraction efficiency of 90% for 'typical' aviation fuels, increased extraction percentages of 92 and 94% results in increases of ~2.3 and 4.6% for the quantified fuel concentration. These differences are generally consistent with the larger measured values for the lower aromatic content fuels (POSF 5018 and 7696) and may explain the offset in the measured values. However, the results from testing with the highest aromatic content fuel (POSF 3602) were not consistent with this trend. A potential hypothesis for the increase was that fuel compounds were being extracted into the aqueous phase, resulting in a higher refractive index (and FSII concentration). This hypothesis was evaluated by performing the D5006 method on FSII-free samples of each fuel; the data collected are shown in Table 9. There was minimal difference between the refractive index of the aqueous extracts and that of water, indicating that extraction of fuel hydrocarbons is not the cause for the higher measured FSII concentrations in fuel POSF 3602.

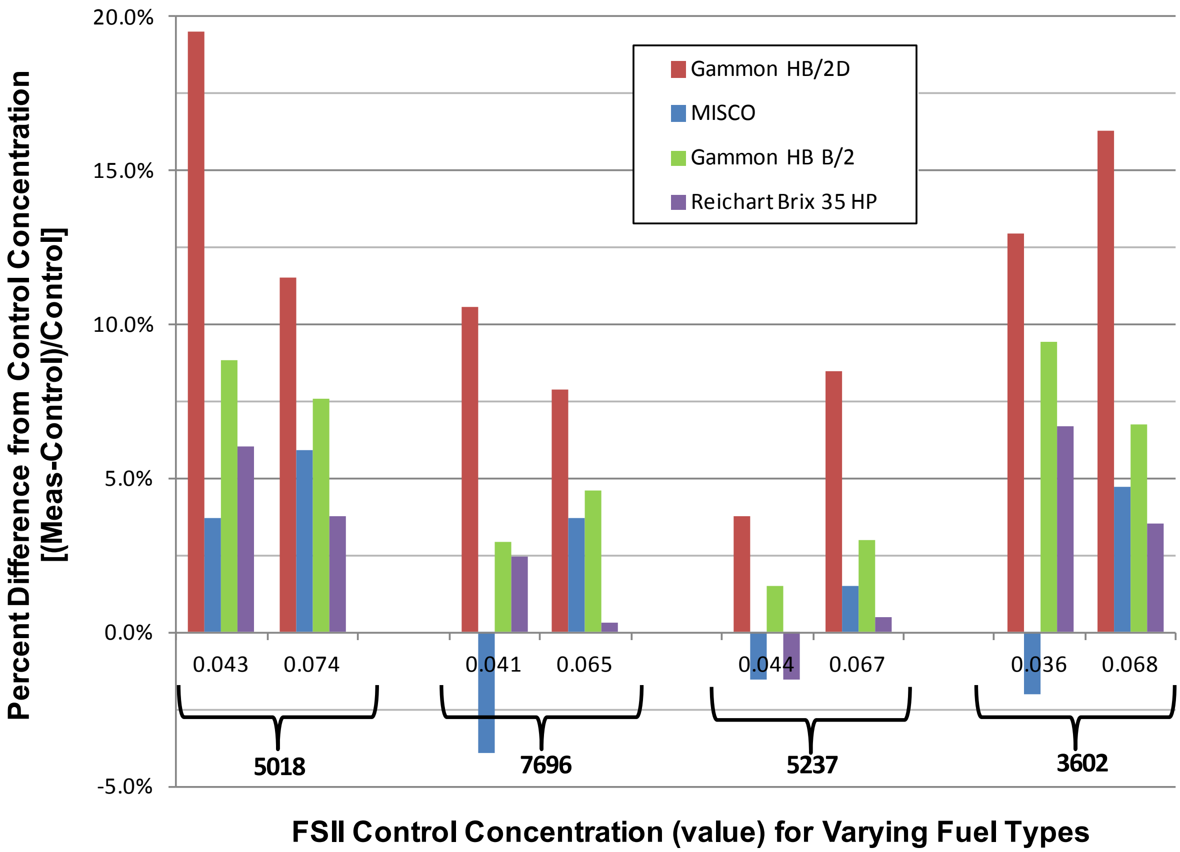

Figure 2: Comparison of Relative Percent Difference between Measured Average FSII Concentration (AFRL and AFPA) as a Function of Refractometer, Control Concentration, and Fuel Type.

Table 5: Results for Testing with Synthetic Paraffinic Kerosene Jet Fuel (POSF 5018).

% FSII Based on Volumetric Preparation	Sample	AR200		Gammon HB 2/D			Misco		Gammon HB B/2	Brix 35HP		GC-MS	FSII in Extracted fuel (%)	FSII Extracted by Water (%)
		nD	*nDTC/20 C*	*nD*	*nDTC/20 C*	*DiEGME*	*nD*	*DiEGME*	*DiEGME*	*Reading*	*DiEGME*			
0.043	**41**	1.336		1.3364	1.3366	0.051	1.33632	0.045	0.050	2.4	0.048	0.042	0.0028	93%
	54	1.3362	1.3363	1.3364	1.3366	0.050	1.33626	0.044	0.050	2.2	0.044		0.0023	95%
	66	1.336	1.3362	1.3364	1.3367	0.052	1.33636	0.045	0.050	2.2	0.044		0.0021	95%
	Average:	**1.3361**	**1.3363**	**1.3364**	**1.3366**	**0.051**	**1.3363**	**0.045**	**0.050**	**2.3**	**0.045**	**0.042**	**0.0024**	**94.3%**
	StDev	**0.0001**	**0.0001**	**0.0000**	**0.0000**	**0.001**	**0.0001**	**0.001**	**0.000**	**0.1**	**0.002**		**0.0004**	**0.9%**
0.043	**48**	1.3361	1.3362	1.3365	1.3365	0.050	1.33631	0.045	0.042	2.2	0.044	0.042	0.0023	95%
	57	1.3361	1.3362	1.3367	1.3368	0.054	1.33628	0.044	0.042	2.4	0.048		0.0023	95%
	Average:	**1.3361**	**1.3362**	**1.3366**	**1.3367**	**0.052**	**1.3363**	**0.045**	**0.042**	**2.3**	**0.046**	**0.042**	**0.0023**	**94.5%**
	StDev	**0.0000**	**0.0000**	**0.0002**	**0.0002**	**0.003**	**0.0000**	**0.001**	**0.000**	**0.1**	**0.003**		**0.0000**	**0.0%**
0.043	**Average:**	**1.3361**	**1.3362**	**1.3365**	**1.3366**	**0.051**	**1.3363**	**0.045**	**0.047**	**2.3**	**0.046**	**0.042**	**0.0024**	**94.4%**
	StDev	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.001**	**0.0000**	**0.001**	**0.004**	**0.1**	**0.002**		**0.0003**	**0.6%**
0.074	**55**	1.3383		1.3386	1.3388	0.083	1.33862	0.079	0.081	3.9	0.078	0.074	0.0052	93%
	42	1.3384	1.3386	1.3387	1.3388	0.083	1.33875	0.080	0.082	3.9	0.078		0.0043	94%
	68	1.3382	1.3384	1.3387	1.3389	0.084	1.33861	0.078	0.081	3.8	0.076		0.004	95%
	Average:	**1.3383**	**1.3385**	**1.3387**	**1.3388**	**0.083**	**1.3387**	**0.079**	**0.081**	**3.9**	**0.077**	**0.074**	**0.0045**	**93.9%**
	StDev	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.001**	**0.0001**	**0.001**	**0.001**	**0.1**	**0.001**		**0.0006**	**0.8%**
0.074	**50**	1.3383	1.3384	1.3387	1.3387	0.082	1.33860	0.078	0.078	3.8	0.076	0.074	0.0048	94%
	58	1.3382	1.3383	1.3386	1.3386	0.080	1.33851	0.077	0.076	3.8	0.076		0.0048	94%
	Average:	**1.3383**	**1.3384**	**1.3387**	**1.3387**	**0.081**	**1.3386**	**0.078**	**0.077**	**3.8**	**0.076**	**0.074**	**0.0048**	**93.5%**
	StDev	**0.0001**	**0.0000**	**0.0001**	**0.0000**	**0.001**	**0.0001**	**0.001**	**0.001**	**0.0**	**0.000**		**0.0000**	**0%**
0.074	**Average**	**1.3383**	**1.3384**	**1.3387**	**1.3388**	**0.083**	**1.3386**	**0.078**	**0.080**	**3.8**	**0.077**	**0.074**	**0.0046**	**93.8%**
	StDev	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.001**	**0.0001**	**0.001**	**0.003**	**0.1**	**0.001**		**0.0005**	**0.6%**

Table 6: Results for Testing with 50/50 Volume Blend of Synthetic Paraffinic Kerosene Jet Fuel and Jet A-1 (POSF 7696).

% FSII Based on Volumetric Preparation	Sample	AR200		Gammon HB 2/D			Misco		Gammon HB B/2	Brix 35HP		GC-MS	FSII in Extracted fuel (%)	FSII Extracted by Water (%)
		nD	*nDTC/20 C*	*nD*	*nDTC/20 C*	*DiEGME*	*nD*	*DiEGME*	*DiEGME*	*Reading*	*DiEGME*			
0.041	**49**	1.3358		1.3360	1.3362	0.044	1.33595	0.039	0.042	2.1	0.042	0.039	0.0032	92%
	53	1.3358	1.3360	1.3360	1.3362	0.045	1.33593	0.039	0.044	2.1	0.042		0.0028	93%
	69	1.3357	1.3360	1.3361	1.3364	0.048	1.33605	0.041	0.046	2.1	0.042		0.0025	94%
	Average:	**1.3358**	**1.3360**	**1.3360**	**1.3362**	**0.046**	**1.33598**	**0.040**	**0.044**	**2.1**	**0.042**	**0.039**	**0.0028**	**92.7%**
	StDev	**0.0001**	**0.0000**	**0.0001**	**0.0001**	**0.002**	**0.00006**	**0.001**	**0.002**	**0.0**	**0.000**		**0.0004**	**0.9%**
0.041	**56**	1.3359	1.3360	1.3361	1.3362	0.046	1.33591	0.039	0.040	2.1	0.042	0.039	0.0029	93%
	63	1.3358	1.3359	1.3360	1.3361	0.044	1.33590	0.039	0.039	2.1	0.042		0.0032	92%
	Average:	**1.3358**	**1.3359**	**1.3361**	**1.3362**	**0.045**	**1.33591**	**0.039**	**0.040**	**2.1**	**0.042**	**0.039**	**0.0031**	**92.2%**
	StDev	**0.0000**	**0.0000**	**0.0001**	**0.0001**	**0.002**	**0.00001**	**0.000**	**0.001**	**0.0**	**0.000**		**0.0002**	**0.5%**
0.041	**Average:**	**1.3358**	**1.3360**	**1.3360**	**1.3362**	**0.045**	**1.33595**	**0.039**	**0.042**	**2.1**	**0.042**	**0.039**	**0.0029**	**92.5%**
	StDev	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.002**	**0.00006**	**0.001**	**0.003**	**0.0**	**0.000**		**0.0003**	**0.8%**
0.065	**43**	1.3375		1.3375	1.3377	0.067	1.33786	0.068	0.069	3.3	0.066	0.064	0.0056	91%
	64	1.3375	1.3377	1.3378	1.3380	0.071	1.33789	0.068	0.071	3.3	0.066		0.0047	93%
	67	1.3375	1.3378	1.3378	1.3380	0.071	1.33789	0.068	0.071	3.3	0.066		0.0043	93%
	Average:	**1.3375**	**1.3377**	**1.3377**	**1.3379**	**0.070**	**1.33788**	**0.068**	**0.070**	**3.3**	**0.066**	**0.064**	**0.0049**	**92.4%**
	StDev	**0.0000**	**0.0000**	**0.0002**	**0.0002**	**0.003**	**0.00002**	**0.000**	**0.001**	**0.0**	**0.000**		**0.0007**	**1.0%**
0.065	**47**	1.3376	1.3376	1.3380	1.3380	0.071	1.33782	0.067	0.065	3.2	0.064	0.064	0.005	92%
	59	1.3375	1.3376	1.3379	1.3380	0.071	1.33786	0.067	0.064	3.2	0.064		0.0054	92%
	Average:	**1.3376**	**1.3376**	**1.3380**	**1.3380**	**0.071**	**1.33784**	**0.067**	**0.065**	**3.2**	**0.064**	**0.064**	**0.0052**	**92%**
	StDev	**0.0001**	**0.0000**	**0.0001**	**0.0000**	**0.000**	**0.00003**	**0.000**	**0.001**	**0.0**	**0.000**		**0.0003**	**0%**
0.065	**Average**	**1.3375**	**1.3377**	**1.3378**	**1.3379**	**0.070**	**1.33786**	**0.067**	**0.068**	**3.3**	**0.065**	**0.064**	**0.0050**	**92.2%**
	StDev	**0.0000**	**0.0001**	**0.0002**	**0.0001**	**0.002**	**0.00003**	**0.000**	**0.003**	**0.1**	**0.001**		**0.0005**	**0.8%**

Table 7: Results for Testing with a High Aromatic Jet A (POSF 3602).

% FSII Based on Volumetric Preparation	Sample	AR200		Gammon HB 2/D			Misco		Gammon HB B/2	Brix 35HP		GC-MS	FSII in Extracted fuel (%)	FSII Extracted by Water (%)
		nD	*nDTC/20 C*	*nD*	*nDTC/20 C*	*DiEGME*	*nD*	*DiEGME*	*DiEGME*	*Reading*	*DiEGME*			
0.036	**51**	1.3354		1.3356	1.3359	0.040	1.33565	0.035	0.040	1.9	0.038	0.036	0.0039	89%
	45	1.3356	1.3358	1.3358	1.3360	0.043	1.33568	0.036	0.041	2.0	0.040		0.0037	90%
	70	1.3355	1.3357	1.3357	1.3360	0.041	1.33568	0.035	0.042	1.9	0.038		0.0033	91%
	Average:	**1.3355**	**1.3358**	**1.3357**	**1.3360**	**0.041**	**1.3357**	**0.035**	**0.041**	**1.9**	**0.039**	**0.036**	**0.0036**	**89.9%**
	StDev	**0.0001**	**0.0000**	**0.0001**	**0.0001**	**0.001**	**0.0000**	**0.001**	**0.001**	**0.1**	**0.001**		**0.0003**	**0.8%**
0.036	**60**	1.3356	1.3357	1.3357	1.3358	0.039	1.33566	0.035	0.038	1.9	0.038	0.036	0.0039	89%
	62	1.3355	1.3356	1.3357	1.3358	0.040	1.33558	0.035	0.036	1.9	0.038		0.0041	89%
	Average:	**1.3356**	**1.3357**	**1.3357**	**1.3358**	**0.040**	**1.3356**	**0.035**	**0.037**	**1.9**	**0.038**	**0.036**	**0.0040**	**88.9%**
	StDev	**0.0001**	**0.0001**	**0.0000**	**0.0000**	**0.000**	**0.0001**	**0.000**	**0.001**	**0.0**	**0.000**		**0.0001**	**0.4%**
0.036	**Average:**	**1.3355**	**1.3357**	**1.3357**	**1.3359**	**0.041**	**1.3356**	**0.035**	**0.039**	**1.9**	**0.038**	**0.036**	**0.0038**	**89.5%**
	StDev	**0.0001**	**0.0001**	**0.0001**	**0.0001**	**0.001**	**0.0000**	**0.000**	**0.002**	**0.0**	**0.001**		**0.0003**	**0.8%**
0.068	**44**	1.3378		1.3385	1.3386	0.080	1.33816	0.072	0.076	3.8	0.076	0.068	0.0079	88%
	61	1.3378	1.3379	1.3382	1.3383	0.076	1.33805	0.070	0.075	3.5	0.070		0.0068	90%
	65	1.3377	1.3380	1.3384	1.3386	0.080	1.33818	0.072	0.073	3.5	0.070		0.0065	90%
	Average:	**1.3378**	**1.3380**	**1.3383**	**1.3385**	**0.079**	**1.3381**	**0.071**	**0.075**	**3.6**	**0.072**	**0.068**	**0.0071**	**89.5%**
	StDev	**0.0001**	**0.0001**	**0.0001**	**0.0002**	**0.002**	**0.0001**	**0.001**	**0.002**	**0.2**	**0.003**		**0.0007**	**0.9%**
0.068	**46**	1.3379	1.3379	1.3386	1.3386	0.080	1.33802	0.070	0.070	3.4	0.068	0.068	0.0081	88%
	52	1.3377	1.3378	1.3385	1.3386	0.079	1.33818	0.072	0.069	3.4	0.068		0.0081	88%
	Average:	**1.3378**	**1.3379**	**1.3386**	**1.3386**	**0.080**	**1.3381**	**0.071**	**0.070**	**3.4**	**0.068**	**0.068**	**0.0081**	**88%**
	StDev	**0.0001**	**0.0001**	**0.0001**	**0.0000**	**0.000**	**0.0001**	**0.001**	**0.001**	**0.0**	**0.000**		**0.0000**	**0%**
0.068	**Average**	**1.3378**	**1.3379**	**1.3384**	**1.3385**	**0.079**	**1.3381**	**0.071**	**0.073**	**3.5**	**0.070**	**0.068**	**0.0075**	**88.9%**
	StDev	**0.0001**	**0.0001**	**0.0002**	**0.0001**	**0.002**	**0.0001**	**0.001**	**0.003**	**0.2**	**0.003**		**0.0008**	**1.0%**

Table 8: Comparison of Method Reproducibility Average, Standard Deviation, and Percent Difference from the Control for the Measured FSII Concentration as a Function of Refractometer, Control Concentration and Fuel Type.

Fuel	Control Conc (%)	GC/MS Conc (%)	Gammon HB 2/D			MISCO			Gammon HB B/2			Brix 35HP			FSII in Extracted fuel (%)		FSII Extracted by Water	
			Average	*StDev*	*% Diff*	*Average*	*StDev*	*% Diff*	*Average*	*StDev*	*% Diff*	*Average*	*StDev*	*% Diff*	*Average*	*StDev*	*Average*	*StDev*
5018	0.043	0.042	0.051	0.001	19.5%	0.045	0.001	3.7%	0.047	0.004	8.8%	0.046	0.002	6.0%	0.0024	0.0003	94.4%	0.6%
5018	0.074	0.074	0.083	0.001	11.5%	0.078	0.001	5.9%	0.080	0.003	7.6%	0.077	0.001	3.8%	0.0046	0.0005	93.8%	0.6%
7696	0.041	0.039	0.045	0.002	10.6%	0.039	0.001	-3.9%	0.042	0.003	2.9%	0.042	0.000	2.4%	0.0029	0.0003	92.5%	0.8%
7696	0.065	0.064	0.070	0.002	7.9%	0.067	0.000	3.7%	0.068	0.003	4.6%	0.065	0.001	0.3%	0.0050	0.0005	92.2%	0.8%
5237	0.044	0.042	0.046	0.004	3.8%	0.043	0.001	-1.5%	0.045	0.004	1.5%	0.043	0.002	-1.5%				
5237	0.067	0.067	0.073	0.002	8.5%	0.068	0.001	1.5%	0.069	0.002	3.0%	0.067	0.001	0.5%				
3602	0.036	0.036	0.041	0.001	13.0%	0.035	0.000	-2.0%	0.039	0.002	9.4%	0.038	0.001	6.7%	0.0038	0.0003	89.5%	0.8%
3602	0.068	0.068	0.079	0.002	16.3%	0.071	0.001	4.7%	0.073	0.003	6.8%	0.070	0.003	3.5%	0.0075	0.0008	88.9%	1.0%

Table 9. Comparison of Water-Phase Refractive Index for Extractions Performed on FSII-Free Fuels.

Extracted Fuel	AR200		Gammon HB 2/D			Misco		Gammon HB B/2	Brix 35HP	
	nD	*nDTC/20 C*	*nD*	*nDTC/20 C*	*DiEGME*	*nD*	*DiEGME*	*DiEGME*	*Reading*	*DiEGME*
None (Water)	1.3327	1.3330	1.3326	1.3330	0.000	1.33297	0.000			
	1.3327	1.3330	1.3327	1.3330	0.000	1.33298	0.000			
	1.3327	1.3330	1.3326	1.3330	0.000	1.33297	0.000			
Ave.:	**1.3327**	**1.3330**	**1.3326**	**1.3330**	**0.000**	**1.33297**	**0.000**	**0.000**	**0**	**0**
5018	1.3327	1.3330	1.3327	1.3330	0.000	1.3330	0.000			
	1.3327	1.3330	1.3326	1.3330	0.000	1.3330	0.000			
	1.3327	1.3330	1.3327	1.3331	0.000	1.3330	0.000			
Ave.:	**1.3327**	**1.3330**	**1.3327**	**1.3330**	**0.000**	**1.3330**	**0.000**	**0.000**	**0**	**0**
7696	1.3326	1.3329	1.3327	1.3330	0.000	1.33300	0.000			
	1.3326	1.3329	1.3327	1.3330	0.000	1.33299	0.000			
	1.3326	1.3329	1.3326	1.3330	0.000	1.33300	0.000			
Ave.:	**1.3326**	**1.3329**	**1.3327**	**1.3330**	**0.000**	**1.33300**	**0.000**	**0.000**	**0**	**0**
5237	1.3327	1.3330	1.3327	1.3330	0.000	1.33303	0.001			
	1.3327	1.3331	1.3327	1.3330	0.000	1.33302	0.001			
	1.3327	1.3330	1.3327	1.3330	0.000	1.33301	0.001			
Ave.:	**1.3327**	**1.3330**	**1.3327**	**1.3330**	**0.000**	**1.33302**	**0.001**	**0.000**	**0**	**0**
3602	1.3328	1.3331	1.3326	1.3331	0.001	1.33306	0.001			
	1.3328	1.3332	1.3326	1.3331	0.001	1.33306	0.001			
	1.3328	1.3332	1.3326	1.3331	0.001	1.33306	0.001			
Ave.:	**1.3328**	**1.3332**	**1.3326**	**1.3331**	**0.001**	**1.3331**	**0.001**	**0.000**	**0**	**0**

5. Summary

The accuracy, repeatability and reproducibility of ASTM D5006 for quantitation of DiEGME at concentrations < 0.10% by volume was evaluated in this study. Measurements were performed over a range of concentrations and in four different aviation fuels to investigate the potential effects of the absolute FSII concentration and fuel composition (primarily aromatic content) on the method quantitation. Control samples with known FSII concentration were prepared and separated into five different blind samples. The blind samples were analyzed by two different operators in two different laboratories, using all refractometers currently approved in D5006. This approach allowed limited evaluation of both the repeatability and reproducibility of the method at reduced concentrations, but required the operators to estimate the measured concentration to three decimal places for the analog refractometers.

It was found that the accuracy and confidence levels for quantitation of low FSII concentrations were substantially better than reported in the D5006 method, with excellent repeatability and reproducibility within and between the two laboratories. A bias to higher quantified concentrations for the 'non-typical' aviation fuels was found during this study. In addition, the fuel composition was found to affect the percentage of FSII extracted to the aqueous phase during analysis, with the extraction percentage decreasing as the aromatic content (or comparable fuel property) increased. This may be the cause for the bias to higher measured values for the two fuels with aromatic contents less than typical petroleum derived aviation fuels (< 15%). However, this does not explain the higher values measured for the high aromatic content fuel in this study. The effect of fuel composition on method accuracy may merit further evaluation, but for typical aviation fuels (15-22% aromatic content), the effect on quantitation may be smaller than the uncertainty of the method. Further evaluation of the accuracy of D5006 at concentrations < 0.10% by volume via a round-robin laboratory study may be necessary for improved statistical analysis.

6. References

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T.O. 42B-1-1, "Technical Manual, Quality Control of Fuels and Lubricants," released 13 August 2012; CHANGE 1 – 19 November 2012.