WHITEPAPER

Precision Comparison Between UVF and MWDXRF for Biodiesel Samples, Renewable Diesel vs. Biodiesel, and the Importance of Oxygen Correction

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Introduction

According to ASTM D6751, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, there are several options for testing sulfur in biodiesel. ASTM D5453 is listed as the referee method, but D7039 may also be used. This paper looks at these methods in more detail using data from the ASTM B100 Proficiency Testing Program (PTP) and, in doing so, also discusses renewable diesel vs. biodiesel and the importance and methodologies for oxygen correction.

Although this paper focuses on ASTM methodology, note that ISO and EN methodologies and specifications are mentioned throughout. For example, EN 14214 is the European Standard for fatty acid methyl esters (FAME), and both ISO 20846 and ISO 20884 are listed as acceptable sulfur test methods.

ASTM B100 PTP Program Overview

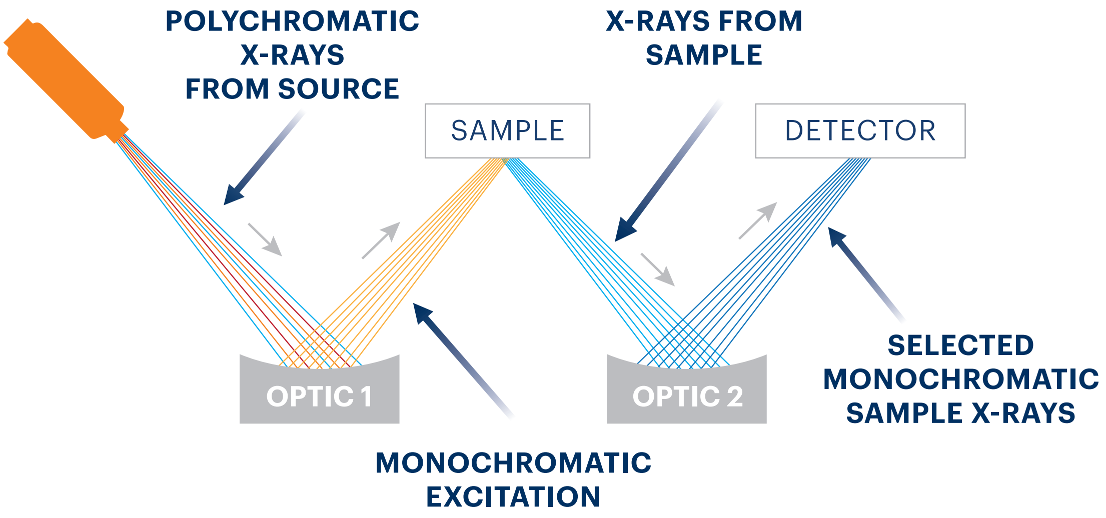
The ASTM B100 PTP allows laboratories to improve their biodiesel testing performance by comparing their biodiesel test results with other laboratories. The statistical analysis also provides a valuable tool to assess test method performance on a particular matrix type and allows comparison between two or more test methods that measure the same property. For the B100 PTP, ASTM sends one-gallon samples out three times per year for analysis of approximately 24 biodiesel properties. This paper will focus on sulfur analysis from 2018 through 2022 using ASTM D5453 and ASTM D7039. First, understanding the test methods is critical to interpreting the data presented.

ASTM D7039 (Monochromatic Wavelength Dispersive X-Ray Fluorescence)

Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF) is a subset of WDXRF that utilizes similar principles. Rather than using filters or traditional crystals that are flat or singly curved, MWDXRF incorporates doubly curved crystal (DCC) optics to provide a focused, monochromatic excitation X-ray beam to excite the sample. A second DCC optic is used to collect the sulfur signal and focus it onto the detector. This modified methodology delivers a signal-to-background ratio that is 10-times more precise than traditional WDXRF, which improves method precision and Limit of Detection (LOD).

D7039 is similar to ISO 20884. However the ISO methodology includes both monochromatic and polychromatic excitation, whereas D7039 specifies monochromatic excitation only.

Figure 1 - MWDXRF Diagram



ASTM D5453 (Ultraviolet Fluorescence)

In Ultraviolet Fluorescence (UVF) technology, a hydrocarbon sample is either directly injected into the analyzer or placed in a sample boat that is cooled and then injected into the high temperature (1000° C) combustion furnace. The sample is combusted in the tube, and sulfur is oxidized to sulfur dioxide (SO_2) in the oxygen-rich atmosphere. A membrane dryer removes water produced during the sample combustion and the sample combustion gasses are exposed to ultraviolet (UV) light. SO_2 is excited (SO_2*), and the resulting fluorescence that is emitted from the SO_2* as it returns to the stable state is detected by a photomultiplier tube. The resulting signal is a measure of the sulfur contained in the sample. ISO 20846 is analogous to D5453.

ASTM Test Method Scope and Precision

Within ASTM test methods, the scope defines the test method parameters, including matrices of interest and range of applicability. The scope is defined by an interlaboratory study (ILS), which also determines the precision (repeatability and reproducibility) of the test method (note: this is a separate study from the PTP program mentioned in this paper). Both ASTM D7039 and D5453 include diesel, biodiesel, and biodiesel blends; see Table 1 for the applicable range of these test methods and precision equations for each test method.

Table 1 - ASTM Test Method Scope and Precision Equations

Method	Scope (ppm)	Repeatability (ppm)*	Reproducibility (ppm)*
D5453	1-400	0.1788 • X^0.75	0.5797 • X^0.75
	>400-8000	0.02902 • X	0.1267 • X
D7039	3.2-2822	0.4998 • X^0.54	0.7384 • X^0.54

*where X is the average of two results

Test method ILS are discrete studies used to define the repeatability and reproducibility of the test method. The advantage of these studies is that they cover multiple sample matrices spanning the entire concentration of the test method. The disadvantage is that these studies are from a discrete point in time, and they typically do not provide in-depth data on a particular sample type. For this information, it is better to look at ongoing ASTM PTP studies, which are organized around a particular sample type, rather than sample properties (test methods). By filtering multiple PTP test cycles for a sample property, one can get an in-depth look at a particular test method(s). So then, let's look at sulfur data from the ASTM B100 PTP program.

What is Precision?

ASTM defines precision in terms of repeatability and reproducibility:

- Repeatability is the difference between successive results obtained by the same operator in the same laboratory with the same apparatus and same test method under constant operating conditions on identical test material
  - A lower repeatability value correlates to a better level of precision and a higher likelihood of obtaining the same or similar test result over multiple measurements of different aliquots of the same sample
- Reproducibility is the difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material
  - A lower reproducibility value correlates to a better level of precision which can minimize risks from inaccurate reporting such as regulatory fines and contract disputes

ASTM B100 PTP Program Results

There were fifteen biodiesel program cycles (or data points) from 2018 through 2022. On average, there are three times as many D5453 participants vs. D7039 participants, though if participants are submitting data using both sulfur methods, this value may be skewed. Only one result is submitted per laboratory for each test method therefore the program statistics cannot include sulfur repeatability. So, the discussion is limited to sulfur reproducibility. The sulfur data and statistics can be summarized as follows:

- Average sulfur concentration ranged 0.18 – 6.70 ppm (Fig 2 line graph and Table 2)
- 47% of D5453 and 60% of D7039 sulfur data points are below the test method scopes (highlighted in yellow on left side of Table 2)
- 57% of the data (0.18 – 1.07 ppm sulfur) has a lower sulfur concentration than its associated reproducibility (Fig 2 data to left of dotted line and highlighted in red in Table 2 on right side)
- Of the remaining 43% data (Fig 2 data to right of dotted line), D7039 has equal or better reproducibility and is biased lower than D5453
- The four XOS reported results with sulfur concentrations within the D7039 method scope (Fig 2 red X's right of dotted line) were closer to the average D5453 sulfur concentration than rest of the D7039 data was

Figure 2 - 2018 - 2022 ASTM Biodiesel PTP Sulfur Data

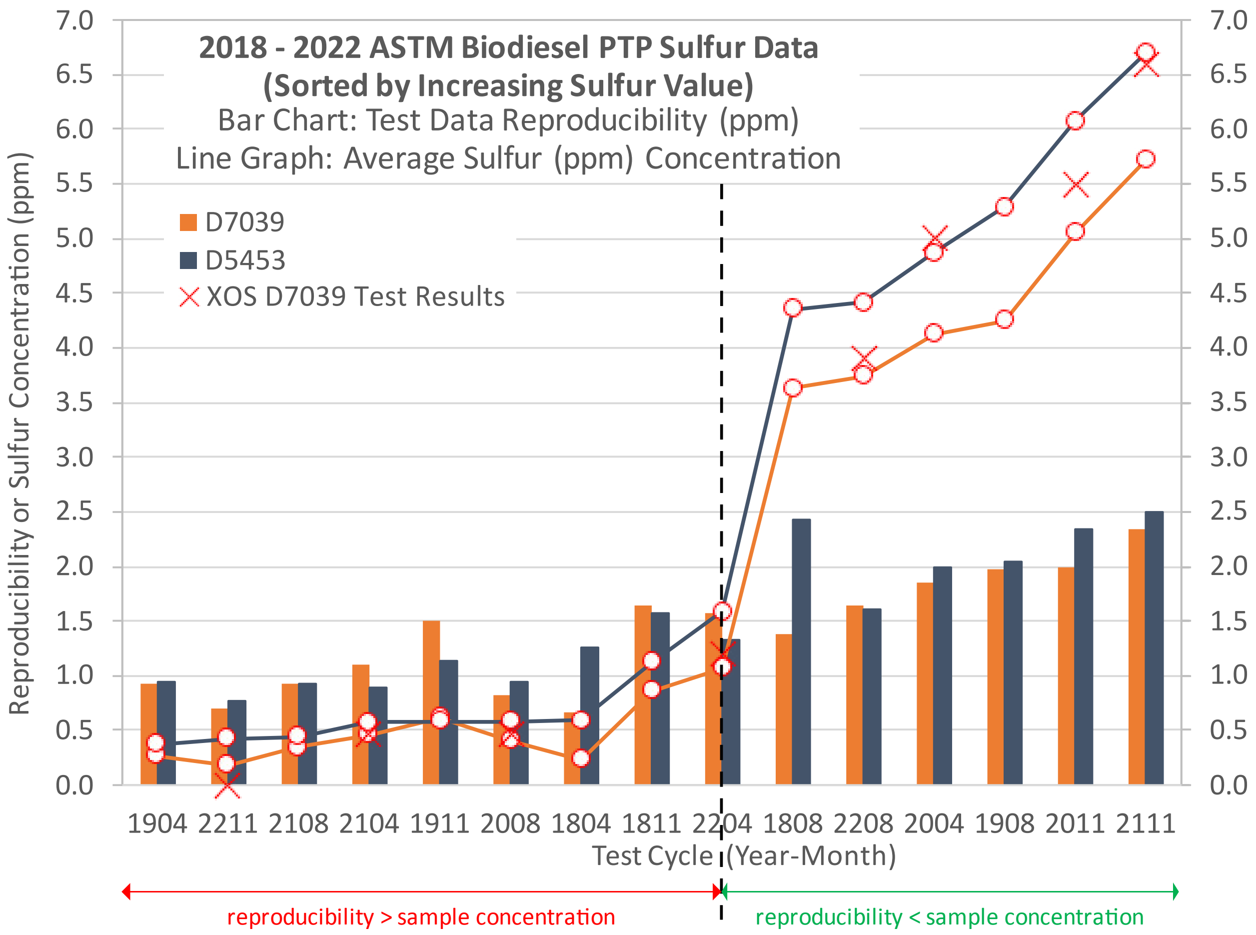


Table 2 - ASTM B100 PTP Sulfur Concentration and PTP Reproducibility (ppm)

Program Cycle Sample Date (Year-Month)	PTP Average Sulfur Concentration (ppm)		XOS D7039 sulfur (ppm) results*	PTP Reproducibility (ppm)	
	D7039	D5453		D7039	D5453
1904	0.27	0.37		0.92	0.95
2211	0.18	0.43	0.00	0.70	0.77
2108	0.35	0.44		0.92	0.92
2104	0.46	0.57	0.47	1.11	0.90
1911	0.62	0.58		1.51	1.14
2008	0.41	0.58	0.47	0.82	0.95
1804	0.23	0.59		0.66	1.26
1811	0.86	1.12		1.65	1.58
2204	1.07	1.59	1.20	1.58	1.33
1808	3.63	4.35		1.39	2.43
2208	3.74	4.41	3.90	1.65	1.60
2004	4.13	4.87	5.00	1.85	1.99
1908	4.25	5.29		1.97	2.05
2011	5.05	6.07	5.50	1.99	2.34
2111	5.72	6.70	6.60	2.35	2.49

*XOS did not join B100 PTP program until January 2020

(yellow) = sulfur concentration below method scope

(pink) = reproducibility > sample concentration

Results Summary

To summarize, this data snapshot suggests that

1. Neither D5453 nor D7039 is suitable for B100 samples ≤ 1 ppm sulfur
2. D7039 has equivalent or better precision than D5453 for B100 samples within the D7039 method scope
3. There is evidence that many PTP D7039 method users are not correcting for oxygen matrix effects, leading to a bias in the results

Renewable Diesel vs. Biodiesel and Oxygen Effects on XRF

Biofuels are any liquid fuels made from renewable biomass, including ethanol, biodiesel, and renewable diesel. Sometimes the terms renewable diesel and biodiesel are used interchangeably, but they are different. According to the **Alternative Fuels Data Center**, renewable diesel is a biomass-derived hydrocarbon that meets the ASTM D975 specification for diesel fuel, and it is produced through various processes such as hydrotreating, gasification, pyrolysis, and other biochemical and thermochemical technologies. Whereas biodiesel is a mono-alkyl ester (or FAME) that meets ASTM D6751 specification for biodiesel, and it is produced via transesterification. In other parts of the world, people may instead refer to EN 14214, specification for FAME, and EN 15940 for paraffinic diesel fuel (renewable diesel).

Another difference between renewable diesel and biodiesel is that biodiesel contains oxygen, typically around 10-12 wt%, whereas finished renewable diesel doesn't contain oxygen and is considered a "drop in" product. Though note that feedstocks for biodiesel and renewable diesel may contain varying amounts of oxygen, depending on the type of feedstock and where in the process the intermediate stream has been sampled.

From an ease-of-use standpoint, drop in products are easy to measure using XRF, as no additional precautions are needed, and the sample can be measured on a typical hydrocarbon calibration. According to D7039 for diesel-like matrices, samples above 2.5% oxygen (biodiesel is typically 10-12 wt% oxygen) will need to be addressed through matrix matched calibration standards or correction factors. ISO 20884 specifies a maximum oxygen content of 3.7%. The high oxygen content in these samples leads to significant absorption of sulfur Kα fluorescence, and if uncorrected, to low sulfur results (see section 5.2 in D7039).

Matrix matching uses calibration standards with the same or similar elemental composition as the samples being measured. For biodiesels, it is possible to make or obtain calibration standards in a biodiesel matrix. However, one should be aware that true biodiesel blanks are difficult to find as they are usually sulfur contaminated. Consider using methyl oleate or octanol for a biodiesel blank as recommended in ISO 20884, instead of the biodiesel blank that comes in the calibration set. Chances are, it's not blank, and it may cause issues when measuring low concentration samples.

For oxygenated feedstocks or samples with varying oxygen content, it may be advantageous to use correction factors instead. ASTM D7039 Table 2 (or Table 3 in this paper) has correction factors for varying amounts of oxygen in biodiesel measured on a mineral oil calibration. The correction factor is applied by multiplying the uncorrected measured result by the correction factor to obtain the oxygen corrected result. Note that the correction factors are limited to D7039 compliant MWDXRF systems such as Sindie and Sindie+Cl. These correction factors can be used when in both 7039 and 2622 modes, because the correction factors in Table 3 are applied to the sulfur ppm values calculated from the total counts-per-second (cps) in 7039 mode or net cps in 2622 mode (after background counts are subtracted), at which time the basic analyzer geometry is identical.

Table 3 - Oxygen Correction Table for Sulfur in Biodiesel on a Mineral Oil Calibration (ASTM D7039 Table 2)

Oxygen, wt%	0%	1%	2%	3%	4%	5%	6%	7%	8%	9%
0%	1.0000	1.0174	1.0348	1.0522	1.0696	1.0870	1.1044	1.1218	1.1392	1.1566
10%	1.1740	1.1914	1.2088	1.2262	1.2436	1.2610	1.2784	1.2958	1.3132	1.3306

NOTE—Determine the correction factor by finding the known oxygen content of the test specimen (for example, 11 wt %) as the sum of the value in the first column and the value in the first row (for example, 11 = 10+1). The intersection of these two values is the correction factor (for example, 1.1914).

Working through a couple of examples, consider two biodiesel samples containing 10 wt% oxygen measured on a mineral oil calibration:

- (uncorrected measured value) x (correction factor) = oxygen corrected value
- 1.0 ppm sulfur (uncorrected) x 1.1740 = 1.2 ppm sulfur (corrected)
- 10.0 ppm sulfur (uncorrected) x 1.1720 = 11.7 ppm sulfur (corrected)

Because the correction factors in Table 3 are multiplicative, as the sulfur concentration increases, the difference between oxygen corrected and uncorrected values is greater, which creates an increasing gap between the measured value and the true value of the sample. A visual representation of this would look similar to the line graph in Figure 2, which suggests that D7039 PTP participants may not be correcting for oxygen matrix effects.

How do we know for sure whether this is the issue? First, if we look at the data from one D7039 participant who is using oxygen correction, we can observe how this participant compares with the rest of the data. The red-X's in Figure 2 represent PTP samples measured at XOS using D7039, a mineral oil calibration, and correcting the measurement result for 10 wt% oxygen. In this instance, it is known that the submitted results were corrected for oxygen, and it can be observed that as the sulfur concentration increases, these results stay more consistent with the average D5453 sulfur concentration than the rest of the D7039 data does.

Secondly, in mid-2022 this paper (in its original form) caught the attention of a task group within ASTM D02.03 (ASTM Committee D02 on Petroleum Products, Subcommittee 3 on Elemental Analysis), and the task group recommended that ASTM poll the B100 D7039 participants to see if and what type of oxygen correction they were performing. ASTM began collecting this information during the August 2022 test cycle, and it turns out that 38-47% of the D7039 participants are not using any method of oxygen correction (see Table 4). In reality this value is likely higher, as 32-43% of participants did not respond to the question on the report form. This information is consistent with version 1 of this paper which predicted that the bias was due to D7039 users not oxygen correcting.

So what does this mean? As seen in Figure 2 (and Table 2), not accounting for oxygen has little effect at and below 1 ppm, but when the concentration is greater than that, so is the average difference. For example, when D5453 results are 5-6 ppm, the D7039 data is biased 1 ppm lower. Since these values are much lower than the 15 ppm US EPA and 10 ppm Euro V/VI diesel sulfur specification maximums, it may not be a concern to some users. However, this will impact test method accuracy. Additionally, when some users are oxygen correcting and others are not, this will also have an effect on test method precision, and this is concerning. If there can be a takeaway from this, it is that it becomes increasingly important to correct for oxygen as the sulfur concentration increases.

Table 4 - Oxygen Correction Methods Used by B100 PTP D7039 Participants

Test cycle	Participants	Matrix Matching*	Correction Factors*	No Correction	Not Reported
2208	21	3	1	**8**	9
2211	19	4	0	**9**	6

* Note: XOS used correction factors for cycle 2211; matrix matching was incorrectly reported.

Conclusion

Despite D5453 being the official referee method for the D6751 B100 specification, data from the ASTM B100 PTP program shows on average that D7039 has equivalent or better precision than D5453. Data from this program also shows that many D7039 participants are not correcting for oxygen content, which not only becomes more important as sulfur concentration increases, but it is likely responsible for the low sulfur bias relative to D5453 seen on the higher concentration samples in this ongoing study.

Additionally, this paper discussed the difference between renewable diesel and biodiesel, and how renewable diesel is a drop in product that complies with the diesel specification and does not require oxygen correction or matrix matching.

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PRODUCT HIGHLIGHT

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