WHITEPAPER

ASTM D5453 vs. D7039 and the Importance of Oxygen Correction for B100 Samples

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Introduction

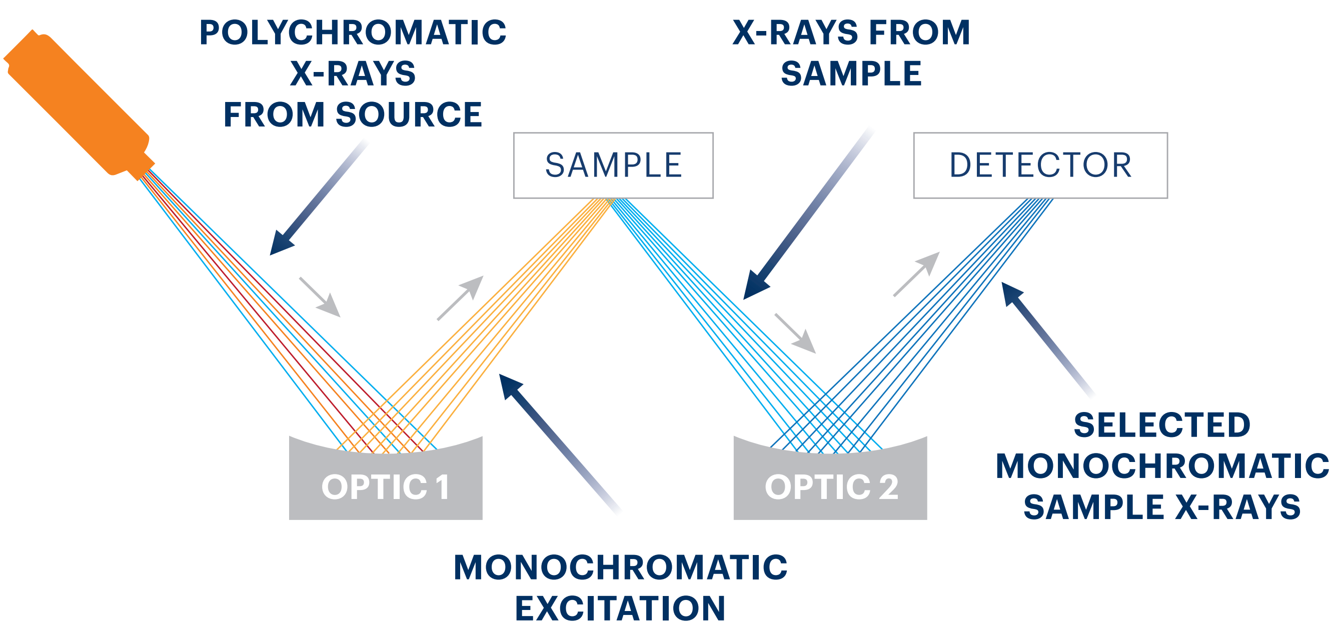
According to ASTM D6751, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, there are several options for testing sulfur in biodiesel. ASTM D5453 is listed as the referee method, but D7039 may also be used. This paper looks at these methods in more detail using 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.

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 2021 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).



ASTM D5453 (Ultraviolet Fluorescence)

In Ultraviolet Fluorescence (UVF) technology, a hydrocarbon sample is either directly injected into a high temperature (1000°C) combustion furnace or placed in a sample boat that is cooled and then injected into the 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.

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 twelve biodiesel program cycles (or data points) from 2018 through 2021. 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 0.27 – 6.70 ppm (Fig 2 line graph and Table 2).
- Approximately half (6 for D5453 and 7 for D7039) of the sulfur data points are below the test method scopes (highlighted in yellow on left side of Table 2).
- 58% of the data (0.27 – 1.12 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 42% data (Fig 2 data to right of dotted line, and Table 2 below dotted line), D7039 has consistently equal or better reproducibility and is biased lower than D5453.
- The three XOS reported results with sulfur concentrations within the D7039 method scope (Fig 2 red Xs right of dotted line, and Table 2 XOS results below dotted line) were closer to the average D5453 sulfur concentration than rest of the D7039 data was.

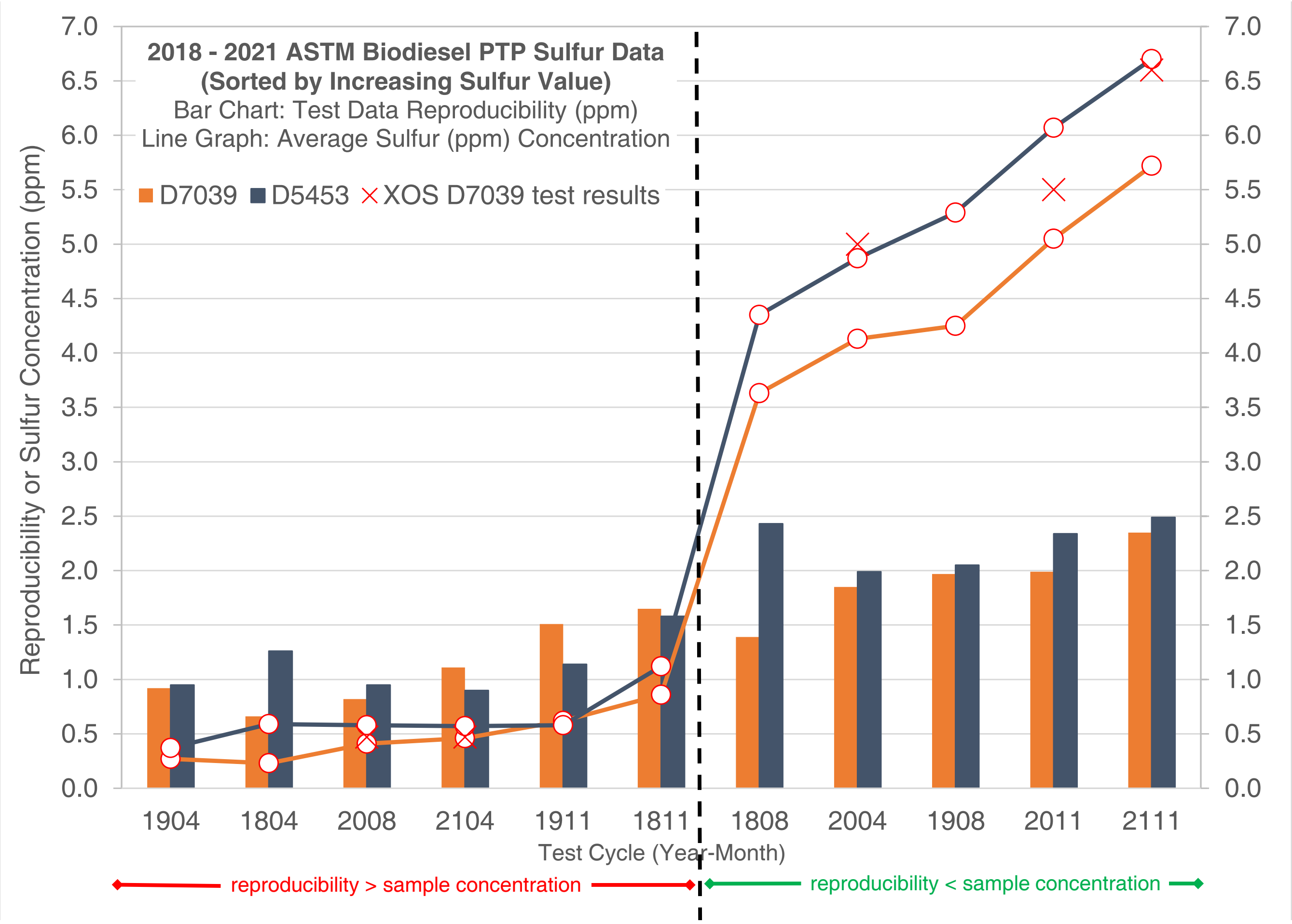


Figure 2. 2018-2021 ASTM B100 PTP Sulfur Data

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)	
	D5453	D7039		D5453	D7039
1904	0.37	0.27		0.95	0.92
2108	0.44	0.35	0.2	0.92	0.92
1804	0.59	0.23		1.26	0.66
2008	0.58	0.41	0.5	0.95	0.82
2104	0.57	0.46	0.5	0.90	1.11
1911	0.58	0.62		1.14	1.51
1811	1.12	0.86		1.58	1.65
1808	4.35	3.63		2.43	1.39
2004	4.87	4.13	5.0	1.99	1.85
1908	5.29	4.25		2.05	1.97
2011	6.07	5.05	5.5	2.34	1.99
2111	6.70	5.72	6.6	2.49	2.35

*XOS did not join B100 PTP program until January 2020

(yellow) = sulfur concentration below method scope

(pink) = reproducibility > sample concentration

So, what does all this mean? In short, 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, and
3. There is some evidence to suggest that PTP D7039 method users may not be correcting for oxygen matrix effects.

It is not surprising that the PTP reproducibility is so poor for B100 samples ≤ 1 ppm sulfur, as this concentration range is at or below the lower limit of both methods. This is because the lower limit of an ASTM method is based on the precision of the interlaboratory study data. And while D7039 has equivalent or better precision than D5453 for B100 samples within the D7039 method scope, it would have been interesting to see the reproducibility statistics for PTP data in the >1-3.5 ppm sulfur range (unfortunately none during this timeframe). More data within this range would have solidified whether D7039 was equivalent or better than D5453, as the lower limit for D7039 is 3.2 ppm.

Lastly, there is limited evidence suggesting that PTP participants using D7039 may not be correcting for oxygen matrix effects. Read on in the next section to discover why.

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 that meets ASTM D6751 specification for biodiesel, and it is produced via transesterification.

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. 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. 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, 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 7039, Sindie 2622, and Sindie+Cl. Also note that these correction factors can be used on a Sindie 2622 and Sindie+Cl 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.

To be clear, we don't know for certain if the bias between D7039 and D5453 is due to oxygen correction issues because D7039 PTP participants do not report their calibration matrix and method of oxygen correction. However, we can surmise this is at least part of the issue based on the red-X's in Figure 2. These red-X's 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. However, this theory is based on limited data from a single user, so it will be interesting to see if this trend continues as more data is collected. If there can be a takeaway from this, it is that it becomes increasingly important to correct for oxygen as the sulfur concentration increases.

Conclusion

Despite D5453 being the official referee method for B100, data from the ASTM B100 PTP program shows that D7039 has equivalent or better precision than D5453 for samples above 3 ppm. Data from this program also suggests that D7039 participants are not correcting for oxygen content, which not only becomes more important as sulfur concentration increases, but it may also be 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.

References:

ASTM D6751-20a, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, ASTM International, West Conshohocken, PA, 2020, **www.astm.org**

ASTM D5453-19a, Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence, ASTM International, West Conshohocken, PA, 2019, **www.astm.org**

ASTM D7039-15a (2020), Standard Test Method for Sulfur in Gasoline, Diesel Fuel, Jet Fuel, Kerosine, Biodiesel, Biodiesel Blends, and Gasoline-Ethanol Blends by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry, ASTM International, West Conshohocken, PA, 2020, **www.astm.org**

ASTM D975-21, Standard Specification for Diesel Fuel, ASTM International, West Conshohocken, PA, 2021, **www.astm.org**

Alternative Fuels Data Center, **https://afdc.energy.gov/fuels/emerging_hydrocarbon.html**, retrieved November 8, 2021

ASTM B100 PTP program landing page, **https://www.astm.org/STATQA/biodiesel.htm**, retrieved November 8, 2021

PRODUCT HIGHLIGHT



16 32.06 Sindie 7039 Sulfur Analyzer

Sindie 7039 complies with ASTM D7039 and ISO 20884 methods and enables fast batch testing from 0.15 – 3000 ppm for sulfur fuel samples at petroleum pipeline terminals, refineries, and test laboratories. This unit is compact with an easy-to-use design requiring minimal maintenance. Sindie 7039 has exceptional signal-to-noise ratio and does not require consumable gases or high-temperature operations.

16 32.06 Sindie 2622 Sulfur Analyzer

Sindie 2622 complies with ASTM D2622, D7039 and ISO 20884 methods, enabling complete flexibility in sulfur analysis. With no compromises in detection, performance and reliability, Sindie 2622 is the ideal sulfur analytical solution from ultra-low sulfur diesel and gasoline to heavy fuel oil and crudes. Utilizing MWDXRF technology, Sindie 2622 offers D2622 method compliance with D7039 performance.

From Ensure Accurate Results for Sulfur & Chlorine Analysis in Biodiesels

The use of biodiesel is rapidly becoming more popular due to growing trends both inside and outside the petroleum industry. The U.S. Energy Information Administration shows that production of biodiesel has increased by over 100 million gallons per month since 2011, with biodiesel making up 4% of total diesel consumption in 20161. Responding to the evolving industry and social landscape, many traditional refineries have begun to incorporate biodiesel into their finished products.

From Get Fast Results for S and Cl in Biofuels in Compliance with ISO 20884 (this new paper should only reference ASTM methods (not ISO)):

The demand for biofuels has increased in recent years and is expected to continue growing through the next decade. In Europe specifically, the EU has made it a priority to have as much as 10% of the total transport fuel from every affiliated country come from renewable sources like biofuel by the year 2020 (1). With over 220 biorefineries in operation across Europe, and new investments in the biofuel and renewables industry In the US is looking to quantify the sulfur in their products in the most efficient and safe way possible. Biorefineries producing biofuels or working with biofeedstocks will still be held accountable for the total sulfur count in their finished products as per ASTM D675.

From Sindie® Online Enables Cost Savings in Biorefinery by Optimising Production with Real-time Results (also relevant info):

The demand for biofuels has increased in recent years, with the EU requiring that 10% of the total transport fuel in its member countries to come from a renewable energy source in 20201. In addition, the U.S. Energy Information Administration anticipates between 18-55% growth in biofuels production over the next 30 years2. While biofuels typically contain little sulfur, they are still required to meet fuel quality compliance specifications either for use in vehicles, or as a blending feed for traditional refinery fuels. As such, biorefineries must measure the sulfur in their product to ensure it is below regulatory limits, typically less than 15 ppm. In addition to this, due to the variety of feedstocks, online analysis of biofuels can be challenging due to changing sample composition.