Chasing the Bias – Gasoline Matrix Matching to Improve ASTM D2622 Sulfur Measurement Accuracy

BACKGROUND

With the implementation of the US EPA Tier III, Euro 5, and upcoming Euro 6 gasoline sulfur regulations (**Table 1**), there is an increasing concern with low-level sulfur data quality. This not only includes analyzer and test method precision, but also bias. ASTM terminology standard D4175 defines bias as "the difference between the expectation of the test results and an accepted reference value". Throughout this paper, we will discuss the bias that is introduced by variations in elemental composition between gasoline, diesel, and mineral oil matrices when measuring sulfur by X-ray Fluorescence (XRF) Spectrometry, specifically ASTM D2622 *(Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry)*. For these sample types, oxygen, carbon, and hydrogen are the elements that contribute to this type of bias. In addition, we will review good calibration techniques and why a weighted least squared calibration is recommended for XOS' Sindie analyzer, and why tightly bracketing the calibration range is not. Lastly, a series of unknown gasoline samples will be measured multiple times with Sindie using a D2622 gasoline calibration to demonstrate typical repeatability for this analyzer.

Gasoline Sulfur Regulation Limits	
Regulation	**Sulfur Maximum**
US EPA Tier III	10 ppm yearly average 80 ppm individual batch maximum
Euro 5 and Euro 6	10 ppm

CHALLENGE

Fuels that contain large amounts of fatty acid methyl esters (FAME) or ethanol, such as biodiesel or gasoline-ethanol blends, have a high oxygen content that leads to significant absorption of sulfur Kα radiation leading to falsely low measurement results when measured on a standard mineral oil or non-oxygenated calibration. So, how much is too much? According to D2622, samples containing more than 25 mass % FAME and 8.6 mass % ethanol will require action to mitigate this interference. Additionally, differences in the carbon-hydrogen (C/H) ratio between the calibration standards (e.g. mineral oil) and samples (e.g. gasoline) may introduce errors in the sample measurement. While D2622 states that it is important to know the C/H ratio, it also states that it is up to the user to decide when this error is large enough to be corrected for.

SOLUTION

D2622 describes three methods to handle elemental interference, including differences in the carbon-hydrogen ratios and that from oxygen:

1. Dilution is not a practical option for gasoline and diesel considering the already low sulfur concentrations of these samples. This is because a sample that is diluted with blank sulfur solvent to mitigate the effect of the interference may also dilute the sulfur concentration below the method detection limit.

SOLUTION CONT.

2. Correction factors can be used to mitigate the effect of elemental sample interferences, however, D2622 does not list specific correction factors within the method because correction factors are apparatus-specific, and there are multiple apparatus types that comply with D2622. A D2622 user will need to contact their instrument manufacturer to determine if there are correction factors that they may use. For example, a Sindie 2622 or Sindie +Cl user may use the correction factors in ASTM D7039, because the apparatus is identical whether in 7039 or 2622 mode.

3. **Matrix matching the calibration standards to the sample type will be our focus throughout this paper. Section 5.3 of D2622 states that "a gasoline may be simulated by mixing isooctane and toluene in a ratio that approximates the expected aromatic content of the samples to be analyzed. Standards made from this simulated gasoline can produce results that are more accurate than results obtained using white oil standards."**

We will explore the effects of matrix matching in more detail by looking at the following test scenarios:

A. Set up a D2622 mineral oil calibration curve and run diesel and gasoline checks to observe the magnitude of the sample-standard bias.

B. Set up a D2622 gasoline calibration curve to see if sample-standard bias is mitigated for gasoline samples.

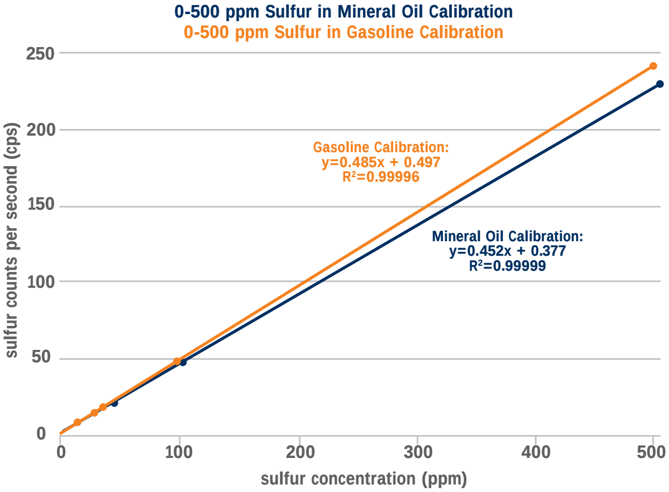
Note: Although we will not discuss oxygen in this paper, D2622 users can use these three mitigation methods to correct for the low measurement bias found in samples containing oxygen.

TEST SCENARIO A: MINERAL OIL CALIBRATION

A 0-500 ppm sulfur in mineral oil calibration curve was set up on a Sindie analyzer according to D2622 using commercially available gravimetrically prepared standards. Each calibration standard was measured for 600s (300s background and 300s sulfur), and standards 100 ppm and less were measured in duplicate using a separate sample aliquot as required in Section 9.2.1 of D2622. These duplicate measurements were averaged before input into the weighted linear squares calibration model. The analyzer demonstrated excellent calibration linearity with a correlation coefficient of determination (R^2) of 0.99999. See **Figure 1** for calibration results.

Note: The blue line represents the mineral oil calibration data.

Figure 1: Mineral Oil and Gasoline Calibrations



A good calibration is essential to minimize systematic error, so be sure to follow these steps to obtain a good Sindie D2622 calibration:

- Use Best Practices to obtain good measurements (visit xos.com/SindieBestPractices)
- Have a good calibration blank, as a bad blank will lead to a high calibration intercept and poor accuracy at the lower end of the calibration range
- Use a new sample aliquot for duplicate measurements (per D2622 methodology)
- Do not tightly bracket the calibration range
- Auto calibration is recommended to obtain a weighted least squares calibration
- Consider matrix matching when necessary to reduce sample-standard bias

Sindie users commonly follow good calibration practices, but many do not understand how weighted least squares work and why it is recommended, as well as why tightly bracketing the calibration range is discouraged.

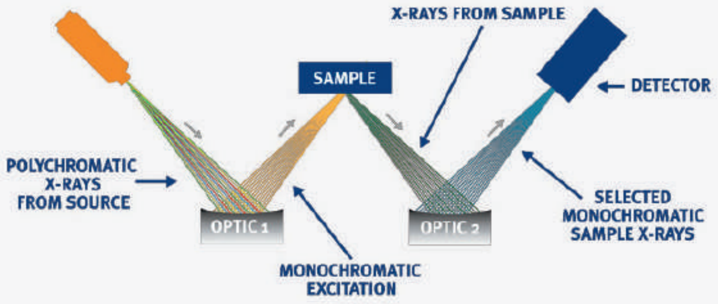
Sindie uses Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF) spectrometry for analysis whether in D7039 or D2622 measurement mode, and the MWDXRF X-ray counting statistics are governed by the Poisson distribution. As a result, the standard deviation on any total number of counts, X, is the square root of the counts, $X^{0.5}$. This is confirmed by the precision of this methodology wherein the precision statement of ASTM D7039 (*Standard Test Method for Sulfur in Gasoline, Diesel Fuel, Jet Fuel, Kerosene, Biodiesel, Biodiesel Blends, and Gasoline-Ethanol Blends by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry*) is essentially represented by a square root function, $r = 0.4998*X^{0.54}$ where X in this case refers to sulfur concentration in ppm. D7039 is used in this example because it exclusively uses MWDXRF technology, whereas D2622 is WDXRF but does not specify excitation type (monochromatic or polychromatic). Additionally, the D2622 method precision is not a square root function ($r = 0.1462*X^{0.8015}$).

The square root function is also used for the Sindie auto calibration model (known as linear weighted least squares). This model assumes a square root relationship between the data value and its error. This means that the model takes into account that the error is not the same on every calibration point, whereas the normal least squares (non-weighted) linear function assumes the same error for every data point regardless of concentration. The non-weighted calibration function does not consider the better absolute precision of the low concentration data and is therefore over-influenced by high concentration data. To combat this, the calibration range of a non-weighted calibration is traditionally tightly bracketed around the range of interest. This also means that multiple non-weighted calibration curves are needed to cover a larger range of interest.

In contrast, the weighted linear model can cover a larger concentration range with one calibration, because higher concentration points do not have this negative effect on the calibration. Moreover, the higher concentration points serve an additional function, which is perhaps more important in this particular application, because the weighted least squares produce a calibration intercept with a lower standard error than that of a non-weighted calibration. These higher calibration points allow the user to take advantage of the better absolute precision at the lower end of the concentration range. Essentially, these higher concentration calibration points, which are usually well above the typical range of interest, will improve the overall calibration in the lower range of interest. Therefore, even though the typical range of interest may be 0-10 ppm, it is recommended to calibrate the Sindie analyzer 0-500 ppm, or even 0-3000 ppm if measuring higher than 500 ppm.

TRUSTED PRECISION WITH MWDXRF

Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF®) utilizes state-of-the-art focusing and monochromating optics to increase excitation intensity and dramatically improve signal-to-background over high power traditional WDXRF instruments. This enables significantly improved detection limits and precision. A monochromatic and focused primary beam excites the sample and secondary characteristic fluorescence X-rays are emitted from the sample. A second monochromating optic selects the sulfur characteristic X-rays and directs these X-rays to the detector. MWDXRF is a direct measurement technique and does not require consumable gasses or sample conversion.



TEST SCENARIO A: CHECK SAMPLE DATA

First, 10 ppm and 15 ppm commercially available gravimetrically prepared sulfur in diesel standards were measured to check the accuracy of the mineral oil calibration. Because both samples are <100 ppm, they were measured in duplicate using separate sample aliquots per the D2622 methodology. The aliquots were measured for 600s each (300s background, 300s sulfur) and the results averaged to produce one D2622 test result. See the check sample results in **Table 2**. From these results, 9.9 ppm and 14.9 ppm, it can be determined that the mineral oil curve is accurate, and that diesel fuel and mineral oil are matrix matched resulting in very little bias.

Table 2. Sulfur (ppm) Check Samples - Mineral Oil Calibration Curve

Sample Type	Accepted Reference Value	Measured Results Repeat 1	Measured Results Repeat 2	D2622 Test Result (ppm)	Bias (ppm)	Actual r (ppm)	D2622 r (ppm)
diesel	10	9.8	10.0	9.9	-0.1	N/A	0.9
diesel	15	14.9	14.9	14.9	-0.1	N/A	1.3
gasoline	10	11.5	10.2	10.8	+0.8	0.1	1.0
gasoline	10	10.7	11.1	10.9	+0.9	0.1	1.0
gasoline	19	21.5	21.0	21.3	+2.3	0.2	1.7
gasoline	19	21.3	20.8	21.1	+2.1	0.2	1.7

Next, 10 ppm and 19 ppm commercially available gravimetrically prepared sulfur in gasoline standards were measured to determine if there is sample-standard bias between gasoline and mineral oil. See the results in **Table 2**. These samples were also measured using a 600s measurement time; however, four aliquots of each sample were measured to produce two D2622 test results to also see what the repeatability is for this sample type with Sindie. While the repeatability for both gasoline samples is very good and within the D2622 method, the bias for the gasoline samples is greater than diesel on the mineral oil calibration. The 10 ppm gasoline sample measured 10.8 and 10.9 ppm, which is an average bias of +0.85 ppm, as compared to the -0.1 ppm bias of diesel fuel measured on the same mineral oil curve. Likewise, the 19 ppm gasoline sample also showed a positive bias, measuring 21.3 and 21.1 ppm on the mineral oil curve.

A positive bias is typical for non-oxygenated gasoline samples measured on a mineral oil calibration. This is due to the differences in carbon and hydrogen content in each of these sample types. The carbon and hydrogen content of a petroleum sample is commonly expressed as a mass ratio, called the carbon to hydrogen ratio, or C/H ratio. The more aromatics and olefins that a sample contains, the higher the C/H ratio. **Figure 1** found in the D2622 standard test method is a graph of the relative sulfur sensitivity vs. C/H ratio.

From this graph, we can see that white mineral oil has a C/H ratio of about 5.7, which is fairly low due to the long-chain paraffinic composition of mineral oil. In contrast, an aromatic chemical such as xylene has a high C/H ratio: 10.5. So, what does this mean? D2622 Section 12.2.1 states that any differences between the C/H ratios of the calibration standards and samples will contribute to the error in the measured result, but it is up to the user's discretion as to when this error is large enough to be an issue.

Many users in the US recently found that this positive bias was large enough to be an issue when performing the accuracy testing portion of the EPA Tier 3 gasoline performance-based measurement system (PBMS) testing (40 CFR 80.47). The PBMS accuracy testing requires that two commercially available standards at two different levels be measured ten times each, and that the average of these measurements should not deviate more than X amount from the accepted reference value (ARV). For ARVs in the range of 1-10 ppm, the deviation limit is X = 0.70 ppm, and X = 1.02 ppm for ARVs in the range of 10-20 ppm. Therefore, if the average of ten measurements at 10 ppm produced an average result of 10.9 ppm, this could be an issue depending on whether the high or low-level accuracy test was being performed. For example, at 19 ppm, if the average of ten measurements is 21.2 ppm, this would fail the high level PBMS accuracy testing.

Outside of the EPA PBMS testing, this will be an issue if a batch of gasoline is produced with a sulfur concentration very near the specification limit. When measured on a mineral oil calibration, this could lead to an inaccurate report of off specification product. Depending on where in the chain of custody this testing occurred, this could result in product reprocessing, contract disputes, or regulatory fines. To avoid this issue, one could produce gasoline at a lower concentration level to ensure compliance, but this will result in sulfur giveaway. The next section will review what happens when these same check samples are analyzed using a gasoline calibration.

TEST SCENARIO B: GASOLINE CALIBRATION AND CHECK SAMPLE DATA

A 0-500 ppm sulfur in gasoline calibration curve was set up on a Sindie analyzer according to D2622 using commercially available gravimetrically prepared standards and the same measurement and calibration protocol that was used when setting up the mineral oil calibration. Again, the analyzer demonstrated excellent calibration linearity, with a correlation coefficient of determination (R^2) of 0.99996 - see **Figure 1** for results.

Note: The orange line represents the gasoline calibration data.

For this test scenario, instead of rerunning the diesel and gasoline check samples, the net intensities (counts per second values) from the previous check sample measurements were reprocessed using the gasoline calibration. This allows one to discretely see the effect of the differing calibration curves on the check sample data, and eliminates any additional measurement uncertainty that may occur when measuring the samples a second time. The reprocessed ppm values can be found in **Table 3**.

Table 3. Sulfur (ppm) Check Samples - Gasoline Calibration Curve

Sample Type	Accepted Reference Value	Measured Results Repeat 1	Measured Results Repeat 2	D2622 Test Result (ppm)	Bias (ppm)	Actual r (ppm)	D2622 r (ppm)
diesel	10	8.9	9.0	9.0	-1.0	N/A	0.9
diesel	15	13.7	13.7	13.7	-1.3	N/A	1.2
gasoline	10	10.5	9.2	9.9	-0.1	0.0	0.9
gasoline	10	9.7	10.1	9.9	-0.1	0.0	0.9
gasoline	19	19.8	19.3	19.6	+0.6	0.2	1.6
gasoline	19	19.6	19.1	19.4	+0.4	0.2	1.6

This reprocessed data demonstrates that matrix matching is effective in reducing or mitigating sample-standard bias for gasoline samples. The 10 ppm gasoline check samples that showed an average +0.85 ppm bias (for two measurements) when run on a mineral oil curve, are now reading 9.9 ppm and effectively mitigating the sample-standard bias. The 19 ppm gasoline check samples also showed a bias reduction, and after reprocessing on the gasoline calibration are 19.6 and 19.4 ppm, reducing the average bias from +2.2 ppm to +0.5 ppm on the two 19 ppm measurements.

This demonstration is important as it shows that bias reduction by matrix matching can improve measurement accuracy. However, this is only one-half of the data quality issue. Next, we will take a brief look at precision (specifically repeatability) of Sindie analyzer using D2622.

D2622 SINDIE PRECISION FOR KNOWN AND UNKNOWN GASOLINE SAMPLES

Within ASTM, the precision of a test method is expressed in terms of repeatability and reproducibility statements. As this study only uses one Sindie analyzer, the precision discussion is limited to repeatability. ASTM D2622 states that repeatability (r) is “the difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material”, and that this “would, in the long run, in the normal and correct operation of the test method exceed the values given only in one case in twenty”. The given repeatability of D2622 is expressed as $r = 0.1462*X^{0.8015}$, where X is the average of two test results. Desirable analyzer repeatability is a numerical value that is equal to or less than the calculated method repeatability for a specific concentration.

As mentioned previously, the 10 and 19 ppm gasoline check samples were measured four times each using a new aliquot each time, so that the Sindie repeatability may be examined and compared to the D2622 test method. The Sindie analyzer repeatability is the difference between two D2622 test measurement results, which can be found in the seventh column of **Table 3**, and the method-calculated repeatability is found in the eighth column. The reprocessed data in **Table 3** illustrates that Sindie exhibits excellent repeatability that is well within the D2622 test method limits. At 9.9 ppm, the calculated method repeatability is 0.9 ppm, whereas the actual analyzer repeatability at this concentration was 0.0 ppm. At 19.5 ppm, the expected D2622 repeatability is 1.6 ppm, whereas the actual repeatability was 0.2 ppm.

Next, three gasoline samples with an unknown sulfur content were obtained, and eight aliquots of each sample were measured on a gasoline calibration to produce four D2622 test results for each sample to look at Sindie repeatability. The samples are labeled A, B, and C, and the nominal sulfur concentrations are 10, 12, and 20 ppm respectively. See **Table 4** for measurement results. In each case, Sindie analyzer demonstrated excellent repeatability that is well within the specified D2622 method repeatability.

Table 4. Sulfur (ppm) in Unknown Gasoline Samples - Gasoline Calibration Curve

Sample	Measured Results Repeat 1	Measured Results Repeat 2	D2622 Test Result (ppm)	Actual r (ppm)	D2622 r (ppm)
A	10.0	9.9	10.0	0.3	0.9
A	9.4	10.0	9.7	0.3	0.9
A	9.7	10.2	10.0	0.2	0.9
A	10.1	10.2	10.2	0.2	0.9
B	11.9	11.6	11.7	0.0	1.1
B	11.5	12.0	11.8	0.0	1.1
B	12.2	11.9	12.1	0.2	1.1
B	11.8	12.0	11.9	0.2	1.1
C	19.4	19.9	19.6	0.6	1.6
C	20.1	20.4	20.3	0.6	1.6
C	20.3	20.4	20.3	0.7	1.6
C	19.5	19.7	19.6	0.7	1.6

CONCLUSION

An accurate measurement combined with good analyzer precision and good calibration techniques will help to ensure quality results. In addition, this will allow refiners to produce product nearer the specification maximum and reduce refining costs. Sindie demonstrates excellent repeatability that is well within the D2622 method. This, combined with the bias mitigating techniques as described, make Sindie an excellent option for testing sulfur in gasoline to US EPA, Euro 5, and Euro 6 regulation limits using ASTM D2622.

PRODUCT HIGHLIGHTS

Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF)

MWDXRF utilizes leading-edge optics technology to produce highly precise monochromatic excitation. This method does not rely on combustion for analysis. With easy to operate instruments, MWDXRF analyzers provide refineries, terminals, and test inspection certification companies with an efficient, reliable, and highly accurate way to determine the sulfur and chlorine content of their products.

Sindie +Cl Sulfur and Chlorine Analyzer

Sindie +Cl delivers exceptional reproducibility for both sulfur and chlorine analysis with one push of a button and zero hassle. Samples are measured directly, which means it can analyze even the heaviest of hydrocarbons like crude oil or coker residuals, without the hassle of boats, injectors, furnaces, or changing detectors. Sindie +Cl complies with ASTM D2622, D7039, D7536, D4929, and SH/T 0842.

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.

Sindie 7039 Sulfur Analyzer

Sindie 7039 G3 delivers excellent precision with an LOD of 0.15 ppm at 300 s. This instrument uses Accucells for hassle-free sample preparation. Sindie 7039 complies with ASTM D7039 and ISO 20884.

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