Best Practices for Improved Sulfur Repeatability

BACKGROUND

There has been an increased need for quality data as petroleum labs around the globe are tasked with adhering to stricter sulfur regulations. With sulfur removal costs in the millions and climbing, refineries can increase overall savings by producing final product closer to the sulfur specification maximum. One way to accomplish this is by reducing variability in sulfur measurements.

CHALLENGE

With many choices for analyzers and analytical techniques on the market, petroleum labs are saddled with the difficult task of determining the best possible approach to ensure their data is of high quality. X-ray fluorescence (XRF) is a technique that is known for its ease-of-use by not requiring injections, sample digestion, or combustion. Within the broader scope of elemental analysis, XRF is seen as having a lower threshold for training technicians.

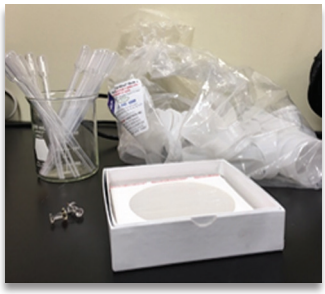
XRF sample preparation, however, is still dependent upon its operators to properly prepare their samples and input the data error-free to ensure that the lab is reporting accurate data. In this paper, we will detail many known best practices for sample preparation using an XOS Sindie +Cl analyzer. The topics covered include cleanliness, measurement time, venting, repeat measurements, and calibration – among others. We will showcase repeatability on Sindie +Cl after using proper sample preparation techniques and walk users through how to ensure their sample data is at its highest possible quality.

BEST PRACTICES

Cleanliness

A clean sample preparation area will ensure there is no cross contamination among samples. It is entirely possible that an XRF cup, for example, coming into contact with a used pipette containing another sample type could have an impact on data integrity. For best results, keep the preparation area clean by following these recommended precautions:

- Keep all materials, such as XRF cups and pipettes, in sealed rather than open containers
- Conduct all sample preparation under a vented hood
- Keep sample film box closed when not in use



BAD

GOOD

In addition to cleaning the sample preparation area, it is especially important to maintain a clean analyzer as well. As multiple samples are run in an analyzer, occasional leaks can build up and become data liabilities. For best results, perform the following tasks daily to ensure your XRF analyzer does not introduce risk to your data:

- Clean the sample plunger and sample basket using isopropyl alcohol (IPA) and a lint-free cloth
- Carefully clean the primary window using IPA and a foam tipped swab (make sure you have a spare primary window before instituting a regular cleaning procedure)

It is important to note that the proper technique for cleaning this area involves first shaking the excess alcohol from the swab. Then, hold the swab parallel to the analyzer surface (rather than perpendicular) and gently swab the primary window film. This will reduce the likelihood of window breakage. Alternatively, use a foam makeup sponge or lint-free cloth to clean the primary window. Use canned or clean compressed air to blow the window dry. Do not shake the canned air prior to use, or this may leave residue on the primary window. If this occurs, repeat the cleaning procedure.

Another precaution to take is to change the secondary window. When changing the secondary window, it is important to use canned or clean compressed air on the sample film to remove any contaminants. Wear gloves and avoid touching the film when securing it. Using four fingers, apply even pressure at equidistant points on the circumference of the snap ring to fasten the window to ensure there are no wrinkles on the film. If the secondary film is wrinkled, repeat the procedure.

Whether you're cleaning the sample preparation area or preparing a sample - you should ALWAYS wear disposable gloves.

Sample Preparation

Proper sample preparation is perhaps the most critical component to improve repeatability. Poor sample preparation and contamination when preparing samples are the primary causes for repeatability issues. Start with a clean sample area and have the necessary sample preparation items nearby.

Use canned or clean compressed air to blow potential contaminants out of the new sample cup. Do not reuse disposable sample cups. Swirl the sample bottle to ensure sample homogeneity, and use a new, disposable pipette to fill the sample cup. Fill the cup at least halfway, more if measuring a viscous sample.

Use canned air on a piece of sample film before placing it on the top of the filled cup. The type of film will depend on the analyzer used – follow the manufacturer's recommendations. Using four fingers spaced equidistant on the circumference of the sample cup collar, press down evenly on the collar to affix it to the sample cup and lock down the sample film. It is important to do a visual inspection to ensure there are no wrinkles in the sample film on the assembled sample cup, as wrinkles can have a negative impact on data quality.

Finally, rotate the sample so that it is face down on a sample stand or lint-free wipe. Under no circumstances should the sample cup sit face down on the bench. Next, use a clean push pin to vent the sample. It is best to avoid venting in the middle on sample cells that have a center well, as this will increase the likelihood of a sample leak which can create contamination issues on the sample plunger. When measuring samples on a Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF) analyzer, it is important to vent all samples (not just volatile samples) to ensure a flat sample film surface when the analyzer lid is closed.

Note: If the analyzer uses XOS' Accucells, the previous sample cup assembly steps are not necessary. For Accucells, pipette 1 ml of sample to fill the pre-vented, preassembled Accucell cup. For laboratories wanting to reduce the potential issues associated with poor sample preparation, consider Sindie Gen3 analyzer which uses Accucell sample cups.

Measurement Repeats & Measurement Time

While many analyzers have software that allows for measurement repeats, Sindie +Cl among them, it is recommended that users prepare separate aliquots for each measurement. With repeat measurements, there is an increased risk that the sample can evaporate, or the film will wrinkle over time – both of these scenarios can have a negative impact on data quality. Additionally, to comply with ASTM D2622, repeat measurements are required on samples containing ≤100 ppm sulfur, and each determination must be made on a new portion of sample material (D2622 Section 10.12).

It is also recommended to prepare samples as they are needed. Preparing multiple samples in advance on a single cell analyzer rather than waiting for the measurement to complete before moving on to the next sample can introduce a contamination risk.

Lastly, follow the recommended measurement time. For best results, measure low concentration samples ≥1 ppm for 300 seconds and samples ≤1 ppm for 600 seconds on Sindie, Sindie +Cl, and Clora. In general, for stable, non-volatile samples, the longer the sample measurement time, the more counts are obtained, and the better the measurement precision.

Once the sample measurement is complete, remove the sample as soon as possible - leaving it in place can increase the risk of sample leaks in the measurement chamber.

Maintenance & Calibration

While routine maintenance on XRF analyzers, such as Sindie +Cl, are minimal in comparison to other analytical equipment, it is still important to incorporate routine analyzer checks. The analyzer should be kept in an optimum state to avoid major problems. One simple action to take is to routinely check the fan filter on the back of the analyzer and clean it off as needed. This will help to avoid dust buildup which can increase the risk of overheating for air-cooled X-ray tubes.

Many labs have incorporated SQC (statistical quality control) checks into their process. The frequency of these checks is often controlled by regulatory testing (e.g. US EPA Tier 3 gasoline) or recommendations of ASTM methodology. Regular SQC checks will indicate when the analyzer is not in statistical control and will reduce the chance of performing product measurements during this time. When the SQC chart is not in statistical control, investigate the cause and recalibrate the instrument if necessary.

Calibration will need to occur after any major analyzer changes or service, such as a replacement of the X-beam. When calibrating MWDXRF analyzers, do not tightly bracket your calibration range. For measuring sulfur in the sub-10 ppm range for gasoline samples, it is recommended to calibrate 0-500 ppm. The reason for this is because Sindie analyzers use a weighted calibration which is extremely linear (as shown in **Graph 1**), and the high points anchor the calibration slope and reduce the standard error of the calibration intercept. Lastly, using matrix matching or correction factors for gasoline samples helps to improve measurement accuracy by reducing or eliminating bias. Gasoline has a slightly high bias (about 1%) when run on a mineral oil calibration. Gasoline with ethanol will bias low on the same mineral oil calibration, due to matrix effects caused by oxygen in the sample. Correction factors for gasoline and gasoline-oxygenated blends measured on a mineral oil calibration can be found in Table 3 of D7039. Note that these correction factors are also applicable to Sindie analyzers run in 2622 mode, because the basic Sindie analyzer geometry does not change when in 2622 mode.

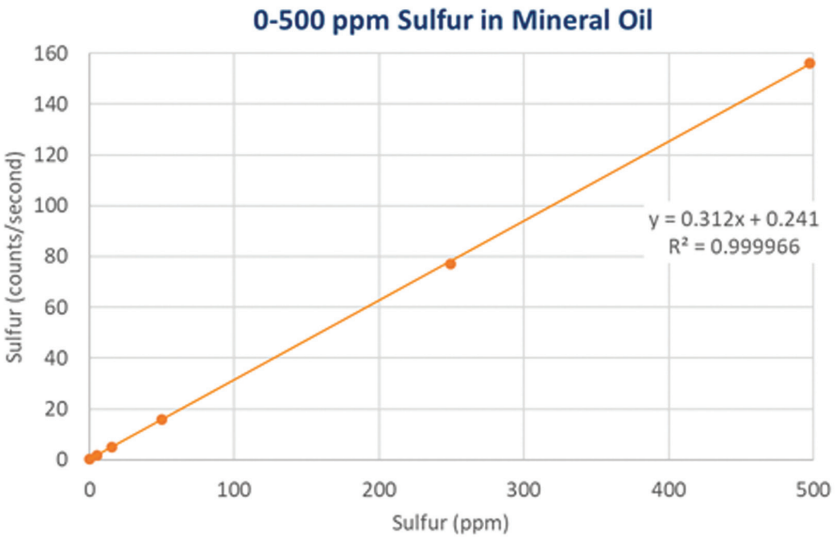
Data Quality

To demonstrate the impact of proper sample preparation, we ran measurements on a Sindie +Cl analyzer. The samples prepared were from commercially-available diesel and gasoline standards. The known concentration values for these samples were 10 ppm for diesel, and 9 ppm for gasoline. Using the best practices stated above, we ran 10 measurements and calculated the average, standard deviation, and relative standard deviation across the measurement data as seen in **Table 1.** The result is a low relative standard deviation below 5%, which demonstrates excellent analyzer consistency and repeatability.

Table 1: Trace Sulfur (ppm) in Fuels

	Diesel	Gasoline
Repeats	Results	Results
1	9.59	8.88
2	9.49	8.15
3	9.53	7.79
4	9.26	8.64
5	9.75	8.51
6	9.00	8.86
7	9.82	8.48
8	9.03	9.17
9	10.49	8.83
10	9.89	8.88
Average	9.59	8.62
Standard Deviation	0.443	0.405
%RSD	4.62	4.71

Graph 1: Sindie +Cl Weighted Calibration



CONCLUSION

XRF analyzers, such as Sindie +Cl, offer petroleum professionals a simplified way to run sulfur measurements without exhaustive sample preparation. By following best practices, operators can mitigate risks of compromising their data and save money by optimizing their production processes.

Did you know?

Do you know the difference between Reproducibility (R) and Repeatability (r)?

Reproducibility (R) = Between lab difference

Reproducibility (R) is the difference between two single independent results obtained by **different operators,** applying the same test method in **different laboratories,** using **different apparatus** on identical test material, would in the long run and in the normal and correct operation of the test method, exceed the value calculated only once in 20 measurements (5% of the time). Or, reproducibility is the maximum expected difference (at 95% confidence) between two measurements taken on the same material using the same test method by two different laboratories each using a different apparatus and operator.

Repeatability (r) = Within lab difference

Repeatability (r) is defined as the difference between repetitive results obtained by the **same operator** in a given laboratory, applying the **same test method** with the **same apparatus**, under constant operating conditions, on identical test material and within short intervals of time, would in the long run and in the normal and correct operation of the test method, exceed the value calculated only once in 20 measurements (5% of the time). Or more simply put, repeatability is the maximum expected difference (at 95% confidence) between two measurement results run on the same material using the same apparatus, test method, and operator.

16 32.06 **Sindie** +Cl Chlorine
Sulfur and Chlorine Analyzer

PRODUCT HIGHLIGHT

Sindie +Cl utilizes a technique known as Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF) – delivering exceptional precision. It delivers trace analysis for both sulfur and chlorine 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 provides refineries, terminals, and third-party testing labs with an easy to use, highly precise elemental analyzer.

METHOD COMPLIANCE: ASTM D2622, D7039, D4929, D7536; SH/T 0842

Authors:
Leslie Johnson - Applications Scientist
Joseph Iaia - Product Manager, Petroleum