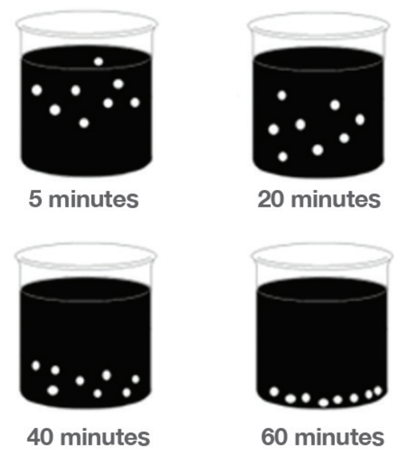
Get Fast D4294 Sulfur Results Without Centrifuging

BACKGROUND

Petroleum professionals looking to certify their products are commonly tied to specific method types for analysis. Two known methods, ASTM D4294 and ISO 8754, utilize a measurement technique known as X-ray Fluorescence, or XRF. Many methods come with their own unique set of interferences and bias corrections. For XRF, a common matrix effect interference involves particulates settling to the bottom of the sample cup and absorbing the X-ray signal. This matrix effect will ultimately influence the total sulfur measurement and lead to a biased result. Refineries and third-party certification companies using XRF for high-particulate samples have relied on centrifuging samples to ensure an accurate sulfur measurement – which involves a time-consuming sample preparation process.

Diagram A: Particulate Settling



CHALLENGE

While many D4294 instruments (traditional XRF) can correct for interfering elements, interferences that settle in crude oil can create challenging scenarios. **Diagram A** demonstrates settling over a period of 60 minutes.

Particulate solids and water have shown to cause underreported sulfur measurements by as much as 40%. Such a significant error can cause misclassification of sour crude oil as sweet crude oil. With global regulatory trends lowering sulfur levels in refined products from diesel to marine fuel, underreporting sulfur may cause refiners to miscalculate the costs associated with processing incoming crude oil. Because D4294 instruments (traditional XRF) take their measurement from the bottom of the sample, settling occurs at the focal point of the analysis rendering the analyzer's automatic interference correction, ineffective. To prevent biased results, many laboratories centrifuge all crude oil samples prior to analysis by traditional D4294 instruments. This increases the amount of processing and time it takes to perform the measurement.

SOLUTION

Many D4294 analyzers are designed with the X-ray detector focused on the bottom of a sample cup where settling occurs, as depicted in **Diagram 1.** Since particulate solids and water settle over time, it is difficult to obtain accurate sulfur measurements due to the changing concentration of interferences. To combat the effects of settling in crude oil, Petra MAX delivers a new, innovative sample chamber that rotates the sample on its side, providing a clear measurement window for more accurate results. See **Diagram 2.**

In the following whitepaper we will discuss how to eliminate the need to centrifuge for D4294 sulfur analysis in two different application studies:

- **Application Study 1: Obtain Accurate Sulfur Results Without Centrifuging in Real-World Samples**
- **Application Study 2: Petra MAX vs Traditional XRF for D4294 Sulfur Analysis**

SAMPLE INTRODUCTION METHODS

Diagram 1: Traditional XRF

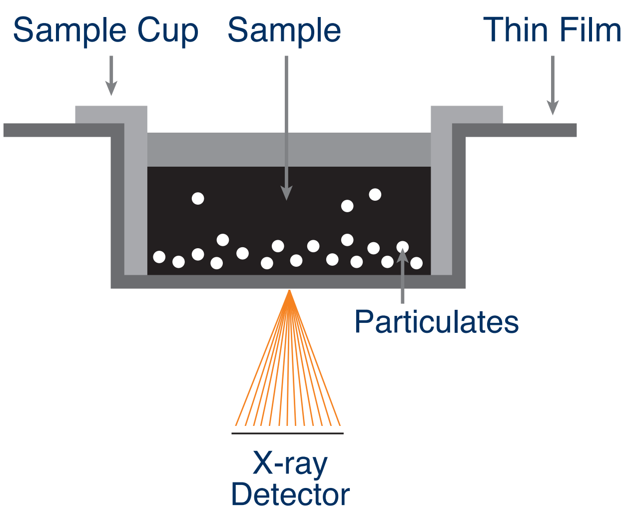
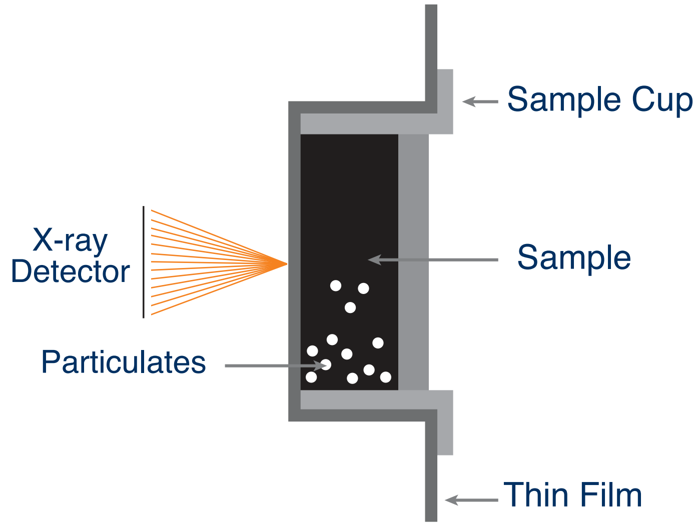


Diagram 2: Petra MAX™



APPLICATION STUDY 1:
OBTAIN ACCURATE SULFUR RESULTS WITHOUT CENTRIFUGING IN REAL-WORLD SAMPLES

In the following application study, we will assess the ability of Petra MAX™ to eliminate the need to centrifuge by running a real-world crude oil sample supplied by a large pipeline. In this paper we will run these samples both with and without centrifuge pretreatment. We will also run the same samples using a traditional XRF analyzer setup, with and without centrifuge pretreatment, and compare the results.

EXPERIMENT

The sample used for this experiment contained an iron concentration of 28 ppm. Samples were prepared by pipetting roughly 8mL of sample into a standard XRF cup after it was dusted off with canned air. Then the cup was sealed using a sheet of Etnom® film which was also dusted off with canned air. Prepped samples were then placed in their respective XRF analyzers and measured for 100 seconds for 3 repeats. We ran each sample 3 times to demonstrate the effects of particulate settling over the duration of the three measurements.

Each sample type was centrifuged prior to preparation of a new sample at a relative centrifugal force (RCF) of 600 for 60 seconds. After, samples were measured for 100 seconds for 3 repeats with both analyzers.

Note: No significant difference was seen in vented versus non-vented samples, as is common with this type of application.

RESULTS

Understanding the Data

The data gathered from the experiments was compiled into several different graphs that showcase various findings. Each graph will be shown and explained with additional data sets. First, we will explore the effects of iron settling in a sample by showing non-centrifuged results on a traditional XRF system. Then we will incorporate data from traditional XRF techniques after centrifuging. Lastly, we will bring in data run on a Petra MAX.

A complete, comprehensive graph **(Graph 4)** can be found at the end of this segment.

The Effects of Settling with Traditional XRF

The data shown in **Graph 1** indicates that there is a direct relationship between the iron concentration, marked by the dotted line, and sulfur concentration when using traditional XRF, marked by the solid orange line as the sample settles over time. The takeaways from this data are:

- As iron settles in the sample cup, sulfur concentration goes down.
- This bias may lead to underreported sulfur.
- Iron settles at different rates.
- With traditional XRF, it is difficult to account for this iron settling without specific sample preparation.

Mitigating Bias by Centrifuging with Traditional XRF

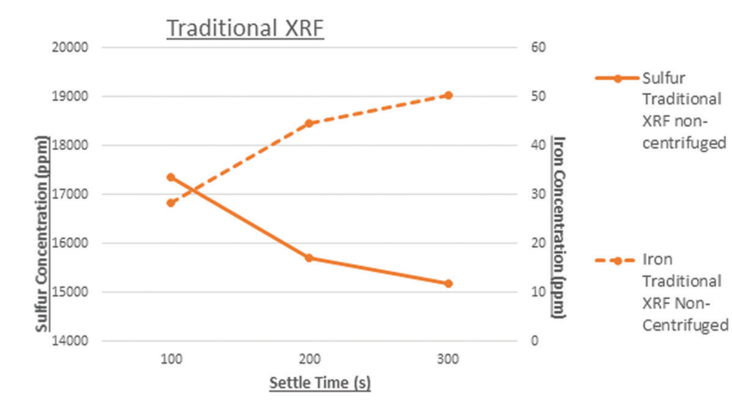
We concluded from our first graph that accounting for this bias without conducting additional sample preparation is difficult in traditional XRF analysis. When using traditional XRF, this is done by centrifuging the sample, which adds preparation. In **Graph 2** we have added in sulfur data for the same sample after centrifuging on a traditional XRF analyzer. The following can be observed:

- The sulfur concentration has mostly stabilized at a higher concentration than the non-centrifuged sample.
- Removal of particulate matter by centrifuging (including iron) mitigates the bias issue.

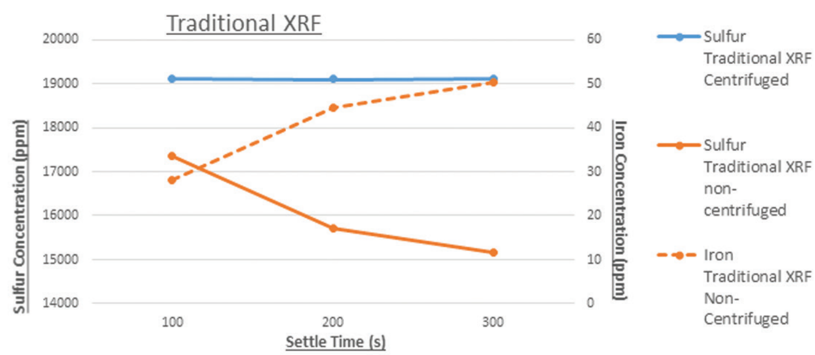
Removing the Need for Centrifuging with Petra MAX

As we have observed, centrifuging is necessary when using a traditional XRF system. What might the data look like when using a Petra MAX analyzer and its vertical sample introduction method? First, we will showcase Petra MAX data on a centrifuged sample in **Graph 3,** which acts as a study control to show that the centrifuged sample data is comparable whether run on Petra or a traditional XRF system.

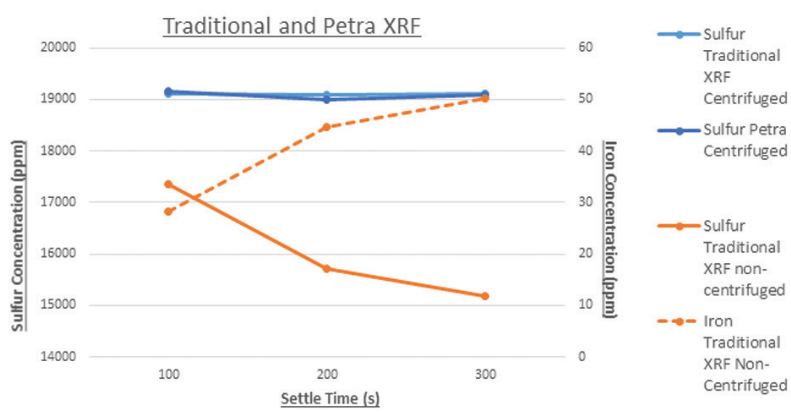
Graph 1



Graph 2



Graph 3

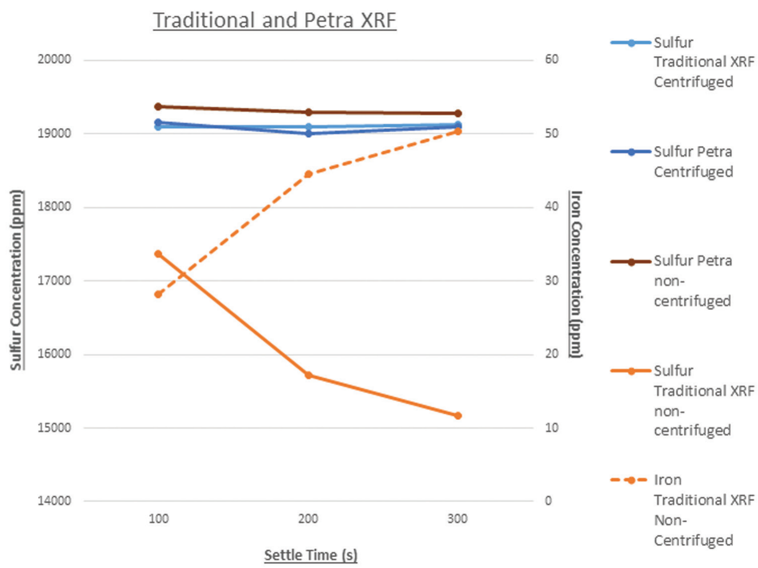


Lastly, to showcase how Petra MAX can eliminate the need for centrifuging, we will display all the data together in **Graph 4.** This combined data brings in results from measurements of the same crude oil sample run on a Petra MAX without centrifuging. The Petra non-centrifuged data shows increased measurement stability over the traditional XRF data (both centrifuged and non-centrifuged) and a slightly higher bias over the centrifuged data (both traditional and Petra XRF).

The increased measurement stability on the non-centrifuged Petra sample vs. traditional XRF is due to Petra's vertical sample introduction system. This orientation mitigates the matrix effects from settling that may occur over the 300s settling time. Particulate matter settles to the bottom of the vertically-oriented sample cup and away from the focal point of analysis, making for a more stable measurement over time.

The slightly higher bias of the Petra non-centrifuged data vs. the centrifuged data is likely due to sample repeatability. The average of the three Petra centrifuged samples is 1.909% and the average of the three non-centrifuged samples is 1.931%. The difference between these samples is 0.022, which is within repeatability at this concentration (r=0.025).

Graph 4



CONCLUSION

Settling can occur quickly and as a result, even highly efficient technicians can run into matrix interferences when using D4294 or ISO 8754 methodology. These interferences can become quite costly as they can lead to misclassification of crudes as sweet or sour.

With the introduction of Petra MAX, professionals can now run crude samples with a higher degree of measurement stability over time and avoid the hassle of centrifuging samples before measurement.

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APPLICATION STUDY 2: PETRA MAX VS TRADITIONAL XRF FOR D4294 SULFUR ANALYSIS

To evaluate the effects of interfering elements, crude oil samples were obtained from three North American refineries. The samples were received in five-gallon drums and then stored in one-liter containers. The iron concentration for each sample was used to estimate the degree of interference. **Table 1** shows a summary of the iron concentration and level of particulate settling for each sample.

Table 1: Crude Oil Classification

	Iron (ppm)	Particulate Settling
Crude A	35	High
Crude B	8	Medium
Crude C	2	Low

TRADITIONAL XRF VS. PETRA MAX

To study the effects of particulate solids on sulfur measurements, a crude oil sample was analyzed using a traditional XRF analyzer and Petra MAX. Refer to **Diagrams 1 and 2** in the beginning of the paper for sample introduction methods. The following sample analysis procedure was performed using both methods:

- A particulate-free certified reference standard of 2 wt% S in mineral oil sample was measured for 100-seconds to check instrument accuracy
- One-liter bottles of crude oil were shaken vigorously, and samples were prepared and measured immediately for 100-seconds

Measurements were repeated 5 times with a 5-second pause in-between. The data was collected and compiled to evaluate the effect of particulate settling on sulfur analysis.

Note: Organosulfur compounds are homogeneous in the sample. Particulates represent elements like Ca, Cl, and Fe.

RESULTS

2% S in Mineral Oil – No Particulates

In order to test the accuracy of each sample introduction method, a particulate-free certified reference standard of 2% sulfur in mineral oil sample was analyzed using both traditional XRF and Petra MAX. Results for both methods demonstrate excellent accuracy. No particulates were present, and all measurements were within 1% of the known sulfur value and met the repeatability requirements for ASTM D4294 and ISO 8754. These results show that in the absence of particulate settling, both sample introduction methods provide accurate results.

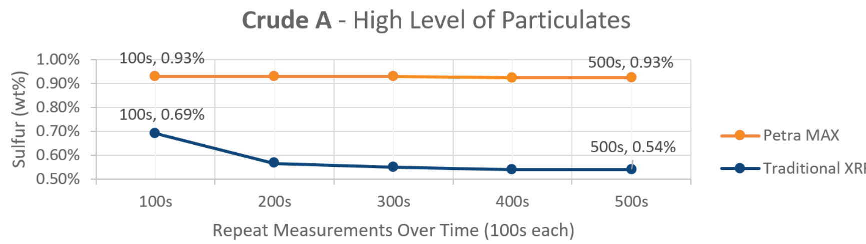
PRODUCT SPOTLIGHT

Petra MAX™ delivers advanced D4294 sulfur analysis in addition to 12 elements from P to Zn including Ni, V, and Fe. This robust benchtop analyzer complies with ASTM D4294 and ISO 8754 for measuring sulfur in hydrocarbons. Petra MAX is powered by HDXRF, utilizing XOS patented doubly curved crystal optics coupled with a high-performance silicon drift detector and an intense monochromatic excitation beam. This industry-leading technology reduces background noise and increases signal-to-noise output, enabling low detection limits and high precision without the need for consumable helium gas, a vacuum pump, or extensive sample preparation.

Crude A - High Level of Particulates

Results for Crude A, containing a high level of particulates, are shown in **Graph 1.** While the traditional XRF results show a rapid drift in sulfur concentration due to particulate settling, the results from Petra MAX remain stable for each repeat measurement. This demonstrates that, even with high levels of particulates, Petra MAX delivers accurate and precise sulfur measurements in crude oil for ASTM D4294 and ISO 8754 methodology.

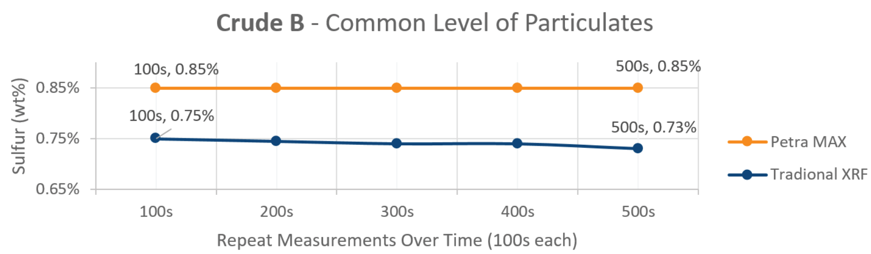
Graph 1: Crude A Results



Crude B - Medium Level of Particulates

The results for Crude B, containing a medium (common) level of particulates, are shown in **Graph 2.** In this crude oil sample, the drift in sulfur concentration for traditional XRF analysis is much less than in Crude A. However, there is a 12% lower sulfur concentration reported by the traditional XRF analysis than Petra MAX, demonstrating that even medium levels of particulate settling still impact the reported sulfur concentration. Petra MAX delivers stable results over the five repeat measurements of Crude B.

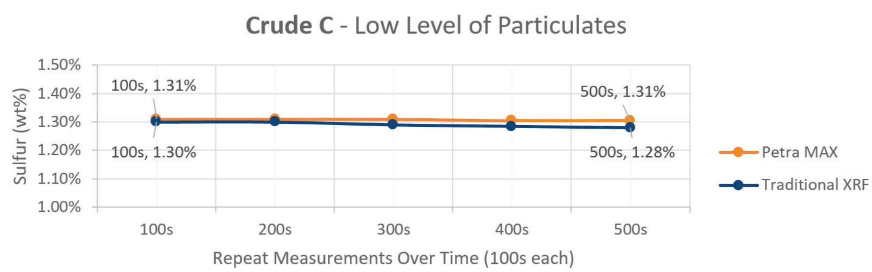
Graph 2: Crude B Results



Crude C - Low Level of Particulates

The results for Crude C, containing a low level of particulates, are shown in **Graph 3.** These results demonstrate that when particulate settling is low, both the traditional XRF and Petra MAX methods show agreement in reported sulfur concentration. This confirms that particulate settling is the cause for underreported sulfur concentrations with traditional XRF analysis.

Graph 3: Crude C Results



RESULTS SUMMARY

Table 2 below shows a summary of the total sulfur drift results of all three crude oil samples from the first to the fifth 100-second measurement, after sitting for 500-seconds. Results from the particulate-free reference standard samples are also included.

Table 2: Total Sulfur Drift Results – Petra MAX vs. Traditional XRF

	CRUDE A High Level of Particulates		CRUDE B Medium Level of Particulates		CRUDE C Low Level of Particulates		2% S in Mineral Oil No Particulates	
Repeats (100s)	Petra MAX	Traditional XRF	Petra MAX	Traditional XRF	Petra MAX	Traditional XRF	Petra MAX	Traditional XRF
#1	0.930	0.690	0.850	0.751	1.304	1.301	2.010	1.995
#5	0.925	0.541	0.848	0.734	1.305	1.285	2.012	1.989
% Drift	0.5%	21.6%	0.2%	2.3%	-0.1%	1.2%	-0.1%	0.3%

All values for Sulfur in wt%

When comparing the results for the particulate-free certified reference sample (2% S in Mineral Oil) between Petra MAX and traditional XRF, there is no drift or bias present. When comparing results for the Crude A sample, there is a significant difference in the reported sulfur concentration. In the initial measurement (repeat #1) for Crude A, the traditional XRF analysis reported 26% less sulfur than Petra MAX. This demonstrates that even if samples were prepared and measured quickly, traditional methods still significantly underreport the sulfur concentration. After the fifth measurement (repeat #5) for Crude A, the traditional XRF analysis reported 42% less sulfur than Petra MAX.

CONCLUSION

In conclusion, crude oil samples with medium to high levels of particulate solids may cause a matrix effect interference of the sulfur signal with traditional XRF when using ASTM D4294 and ISO 8754 methodology. Because settling can happen very quickly, even rapid sample preparation and measurement cannot prevent underreported sulfur in crude oils that exhibit particulate settling.

Increased availability of crude oils with properties at the extreme end of the API scale, like light shale oils and heavy crude from oil sands, has increased the blending of crude oils in order to attain desirable properties that match refinery-operating requirements. This study demonstrates that matrix effects from particulate settling can affect reported sulfur results by as much as 40% in traditional D4294 analysis, which will likely lead to misclassifying sweet and sour crude oil.

The new Petra MAX sample introduction technique eliminates the matrix effects altogether, and offers a more efficient process compared to centrifuge pretreatment. As demonstrated throughout this study, Petra MAX delivers stable results regardless of the level of particulates in the crude oil.

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