

IMPACT OF TIER 3 PROGRAM

Tougher regulations are challenging refiners to produce higher quality products while trying to maximize efficiency. The U.S. Environmental Protection Agency (EPA) is enacting Tier 3 requirements that will begin in 2017 requiring sulfur levels in gasoline to be 10 ppm or lower. Increased Hydrotreating and modifying crude slate are some of the levers that can be pulled to help lower sulfur levels in finished products. Hydrotreating catalyst life depends on the feed and operation of the unit. Increased monitoring will be critical in meeting these requirements and maximizing efficiency. WDXRF has proven to be a fast, easy, and precise method to measure sulfur in hydrocarbon streams.

Beginning in 2017, the EPA will begin enforcement of the Tier 3 Regulations on Gasoline. Current Tier 2 regulations allow an annual average standard of 30 ppm sulfur in gasoline which will be lowered to 10 ppm on January 1st, 2017. In order to meet these lower sulfur levels, refineries must invest in new or upgraded equipment, modify operations or a combination of both. Regardless, it will increase the cost of producing gasoline. US refiners have had more choices of crude types in recent years. Heavy, sour crude provided cost advantages as these were

priced lower. Refiners modified equipment and operations to accommodate the cheaper crude. Figure 1, illustrates the trend of US sulfur content and API Gravity from 1985 through 2015. Crude trended heavier and sulfur content increased as technology improvements were made to suit these cost-effective feedstocks. Advances in drilling techniques led to readily available Light Tight Oils to serve the refining market and lessen dependence on less stable crude sources. Although these feeds were lighter and had little sulfur, they pose other challenges to refiners. Specifically, they tend to be high in waxes and are prone to fouling.

As crude sulfur levels increased, refiners invested heavily in sulfur removal. This was done to capitalize on the cheaper high sulfur crude as well as meet increasingly stringent sulfur specifications on finished products. Between 1985 and 2015, desulfurization capacity nearly doubled from 8.9 Million Barrels per Stream Day to over 17.3 Million Barrels per Stream Day. Figure 2, shows the relationship between US crude sulfur levels and US refinery desulfurization capacity.

For the implementation of Tier 3 regulations, refiners are looking at increasing desulfurization at the fluid catalytic cracking unit (FCCU). The entire feed can be pre-treated or the gasoline can be post-treated or a combination of both. Careful consideration must be given to factors such as hydrogen availability, heat balance, catalyst type, incoming sulfur content, feed nitrogen content, and planned cycle life. Pre-treating feed provides several advantages for sulfur removal. Pre-treating will remove metals and nitrogen, which are poisons to the FCCU catalyst. Additional hydrogenation from pre-treating will increase conversion in the FCC process. Conversely, pre-treating can be very expensive and may not be possible due to heat or hydrogen limitations. Post-treating the gasoline stream may be an easier option, although there is significant reduction of octane in the process. FCCU gasoline contains valuable olefins that contribute to the octane. Post-treatment will reduce the octane number of the gasoline by conversion of valuable olefins, which must be supplemented by reformate.

For every part per million of sulfur removed, a refinery spends significant money on capital, hydrogen, catalyst, and energy. The related downtime to catalyst change out must also be factored into the equation. Catalyst has a finite life, and that length of time is dictated by how the Hydrotreater is operated. By varying temperature, space velocity, and hydrogen partial pressure, sulfur removal and catalyst life are impacted. Crude slate can be modified to reduce total sulfur content and reduce strain on sulfur removal equipment. Crude swaps come at a cost, either in the form of higher purchase price, creating problems on other refinery units, or product yield.

Regardless of what method is utilized to produce gasoline at these lower sulfur levels, monitoring sulfur levels will be critical in controlling costs. Optimization is dependent on knowing the sulfur levels at all times, accurately and reliably.

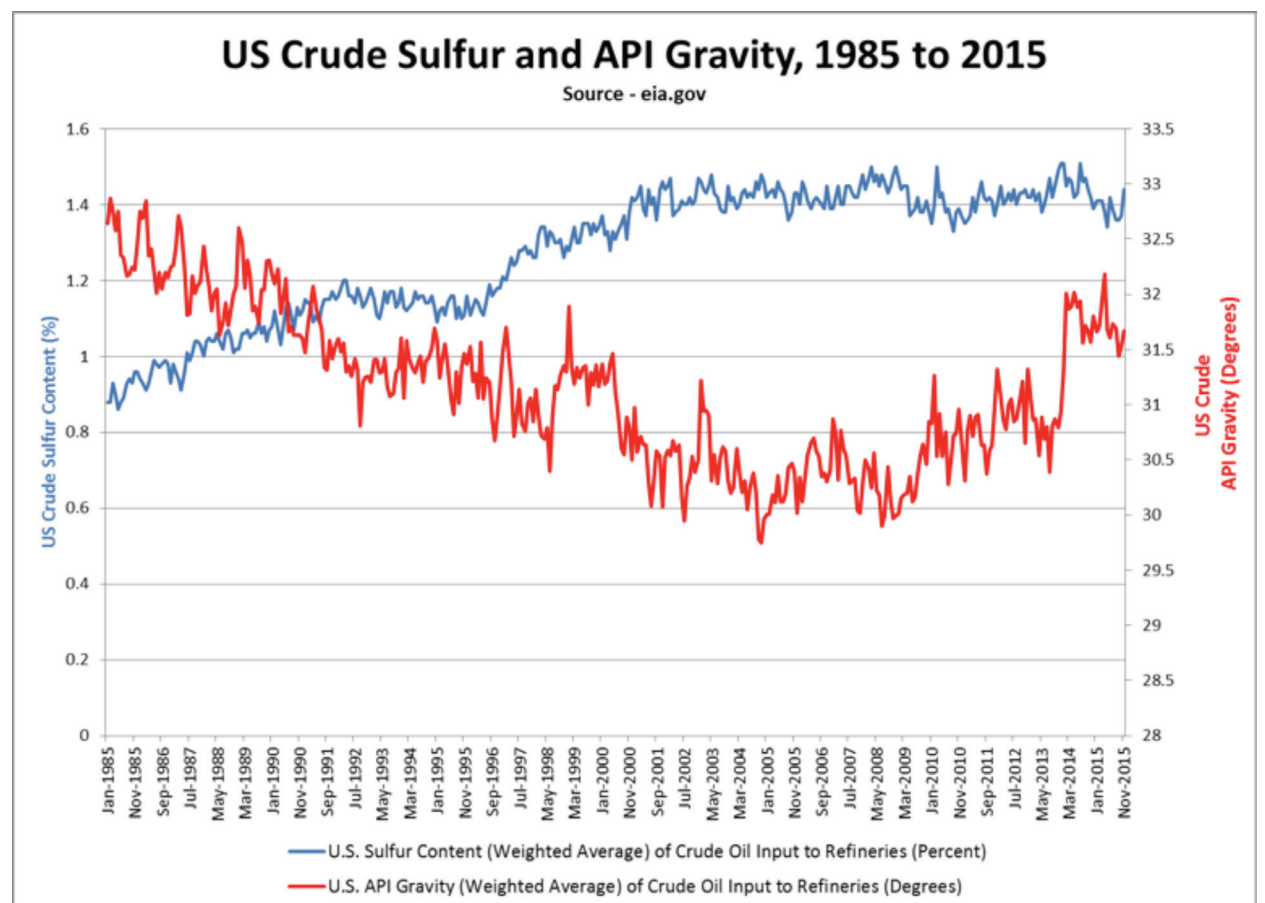


Figure 1. US Crude Quality (Sulfur Content and API Gravity) – EIA.GOV.

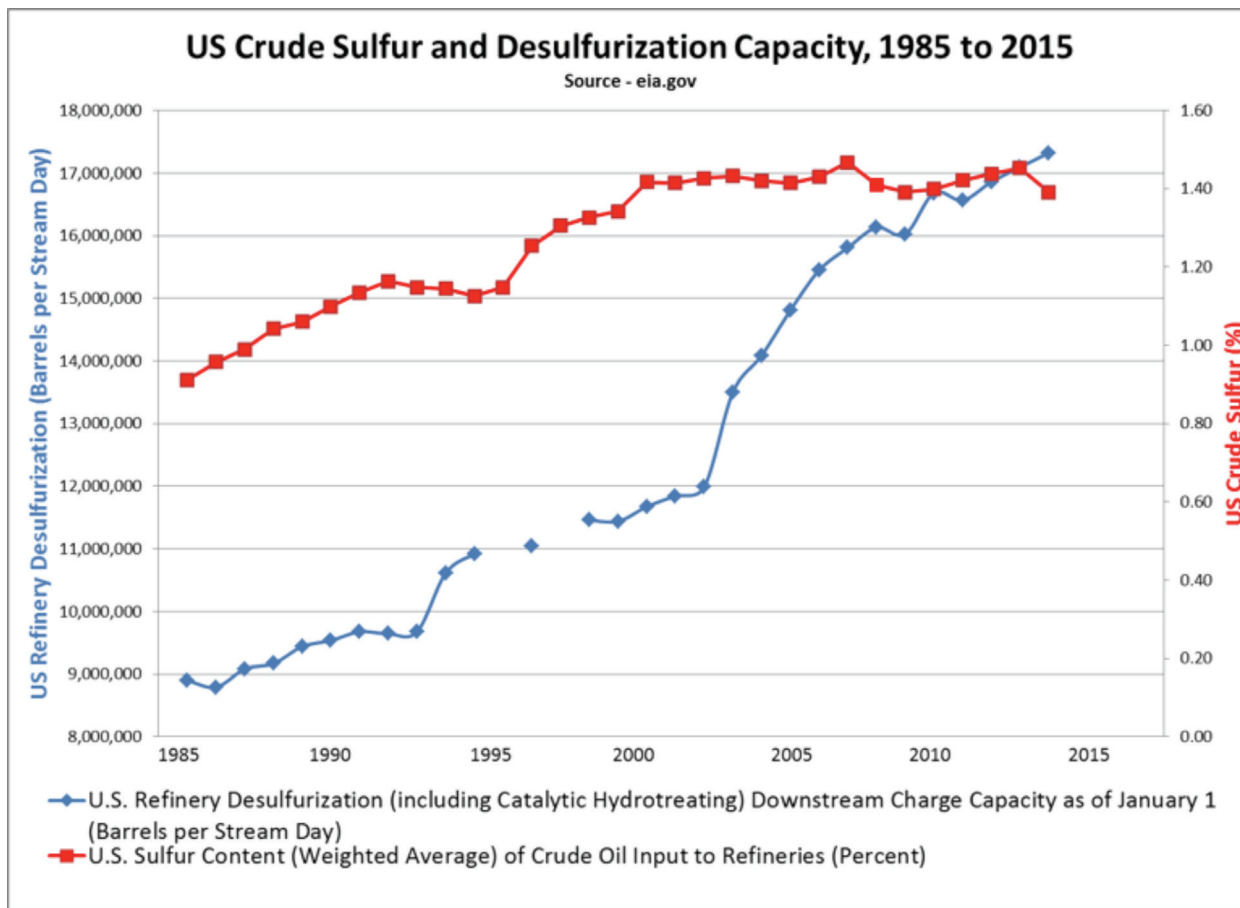


Figure 2. US Crude Sulfur Content and Desulfurization Capacity – EIA.GOV.

Total Sulfur Methodologies and Technologies

There are a number of different technologies available on the market for testing sulfur in liquid petroleum products, due to regulations and requirements around the world. Shown below is a table outlining the different relevant technologies and their correlating methods. Process analyzers based on these technologies typically correlate to the respective laboratory method, or in some cases may have a method of their own.

Table 1. Total Sulfur Methods

ASTM Method	Technology	Range	Scope Fuel Types
D2622	WD XRF	3 ppm - 4.6 wt. %	Diesel fuel, jet fuel, kerosene, other distillate oil, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, gasoline-ethanol blends, and biodiesel
D4294	ED XRF	17 ppm - 4.6 wt. %	Diesel fuel, jet fuel, kerosene, other distillate oil, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, gasoline-ethanol blends, biodiesel, and similar petroleum products
D5453	UVF	1.0 - 8000 ppm	Liquid hydrocarbons, boiling in the range from approximately 25 to 400°C, with viscosities between approximately 0.2 and 20 cSt at room temperature. Including naphtha, distillates, engine oil, ethanol, FAME, and engine fuel such as gasoline, oxygen enriched gasoline (ethanol blends, E85, M85, RFG), diesel, biodiesel, diesel/biodiesel blends, and jet fuel.
D7039	MWD XRF	3.2 – 2822 ppm	Gasoline, Diesel Fuel, Jet Fuel, Kerosene, Biodiesel, Biodiesel Blends, and Gasoline-Ethanol Blends

In this paper, we will discuss the performance and precision of the D7039 method using MWD XRF technology. This technique utilizes high performing doubly curved crystal (DCC) optics coupled with a low power X-ray tube creating a low maintenance, highly precise technology. MWD XRF is a simplified and highly robust X-ray technique which provides sub-1 ppm sulfur detection. An MWD XRF analyzer engine (Figure 3) consists of a low power X-ray tube, a point-to-point focusing optic for excitation, a sample cell, a second focusing optic for collection and an X-ray detector. The first focusing optic captures a narrow bandwidth of X-rays from the source and focuses this intense, monochromatic beam to a small spot on the sample cell. The monochromatic primary beam excites the sample and secondary characteristic fluorescence X-rays are emitted. The second optic collects only the characteristic sulfur X-rays and focuses them on the detector. The analyzer engine has no moving parts and does not require consumable gasses or high temperature operations. MWD XRF removes the scattered background peak created by the x-ray tube increasing the signal-to-background ratio (S/B) by a factor of 10 compared to conventional WD XRF technology. The S/B is improved by using the monochromatic excitation of the x-ray source characteristic line. Additionally, the focusing ability of the collection optic allows for a small-area x-ray counter, which results in low detector noise and enhanced reliability.

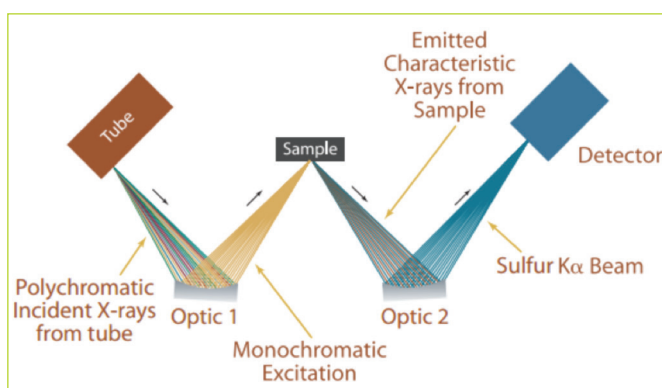


Figure 3. Typical MWD XRF Setup

The WDXRF technique has been accepted practice for measuring sulfur in petroleum liquids for many years. However, when regulations for highway diesel moved to less than 15 ppm at the point of use, mandated by the EPA in 2006, improvements to the analytical instruments and revision to the method was required in an effort to remain competitive with emerging techniques. Similar evolution of the UVF method has taken place while EDXRF has not yet established itself as a viable ultra-low sulfur measurement technique. MWDXRF, on the other hand, was developed specifically to address the need of refiners and petroleum distribution partners for a simple measurement technique, ideally suited for single element, ultra-low sulfur measurements.

The D7039 method (MWDXRF) is essentially a subset of D2622 (WDXRF) with some important distinctions. The excitation X-ray beam of a WDXRF instrument is polychromatic whereas the MWDXRF excitation beam is monochromatic. For both, the output of the X-ray tube comprises the characteristic energy of the target element and the Bremsstrahlung spectral energy associated with the production X-rays by electron acceleration in a vacuum tube. The target element is chosen for a characteristic X-ray just high enough in excitation energy to produce X-ray fluorescence of the element of interest (sulfur) but low enough to minimize background scattering.

WDXRF instruments aim the multi-energy beam at the sample and the resulting beam is typically collimated and aimed towards a diffraction crystal, where it is then diffracted to a detector. Acting as a filter, the diffraction crystal is selected and physically arranged to direct the characteristic X-rays of the element(s) of interest towards the detector. The detector sees a spectral background with distinct peaks associated with the element(s) of interest rising above the background.

MWDXRF instruments, on the other hand, direct the excitation beam to a doubly curved crystal (DCC), selected and aligned such that the maximum beam flux is captured and only the characteristic energy of the target is diffracted towards the sample. Figure 4, below illustrates the Polychromatic (left side) and Monochromatic (right side) excitation beams. With the DCC, the monochromatic excitation is a highly focused, single energy beam incident for the sample. This in turn results in a cleaner fluorescence signal of the sample with far less scattering, which is then directed to another doubly curved crystal for selecting only the characteristic energy of the element of interest to be diffracted to the detector. The end result is a single energy peak with very little spectral background. This is what delivers a signal-to-background ratio improved by a factor of 10 over WDXRF. It also allows use of a much lower power X-ray tube. Figure 5 illustrates the impact of the second DCC.

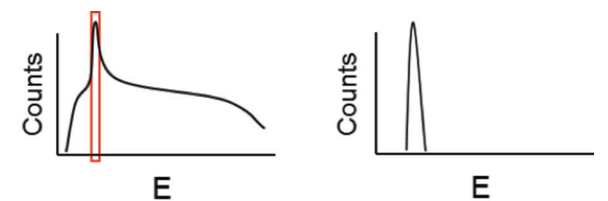


Figure 4. Polychromated (left) and Monochromated (right) Beams

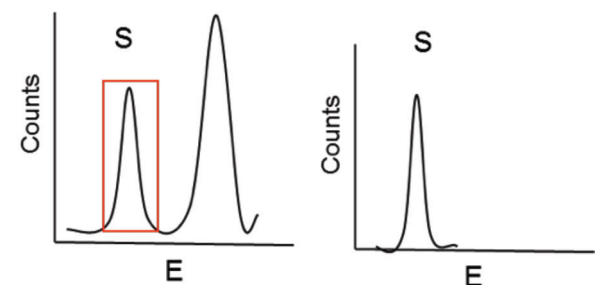


Figure 5. Fluorescent Signal Before DCC (left) and after DCC (right)

For both techniques, the detector can be a proportional counter and a pulse height analyzer is required. In the case of MWDXRF, the pulse height analyzer can consist of an integrated pre-amplifier/amplifier/ single channel analyzer, since only a single energy appears in the spectrum.

Value of Precision

American Society for Testing and Materials (ASTM) methods such as D7039 are required to include full precision statements that include a repeatability and reproducibility component. Repeatability (r) is the variation of two measurements within a 95% confidence interval taken on one instrument of the same sample under the same operating conditions. Reproducibility (R) is the variation of running the same sample at different test sites using similar equipment. The ASTM D7039 precision statement was updated in 2013 to include a repeatability (r) for all products of $0.4998 * X^{0.54}$ and a reproducibility (R) for all products of $0.7384 * X^{0.54}$. With process instrumentation, reproducibility becomes critical. If the process can be continuously and quickly monitored, variation can be identified and optimization can be handled. As compared with the other methodologies in Table 1, D7039 offers superior reproducibility from 5-10ppm which is critical for the Tier 3 mandate. As seen below in Figure 6, MWDXRF provides better reproducibility at the Tier 3 levels of 10 ppm sulfur in reformulated gasoline. This R value can help a refiner justify the economics of installation quickly when process optimization can be achieved faster.

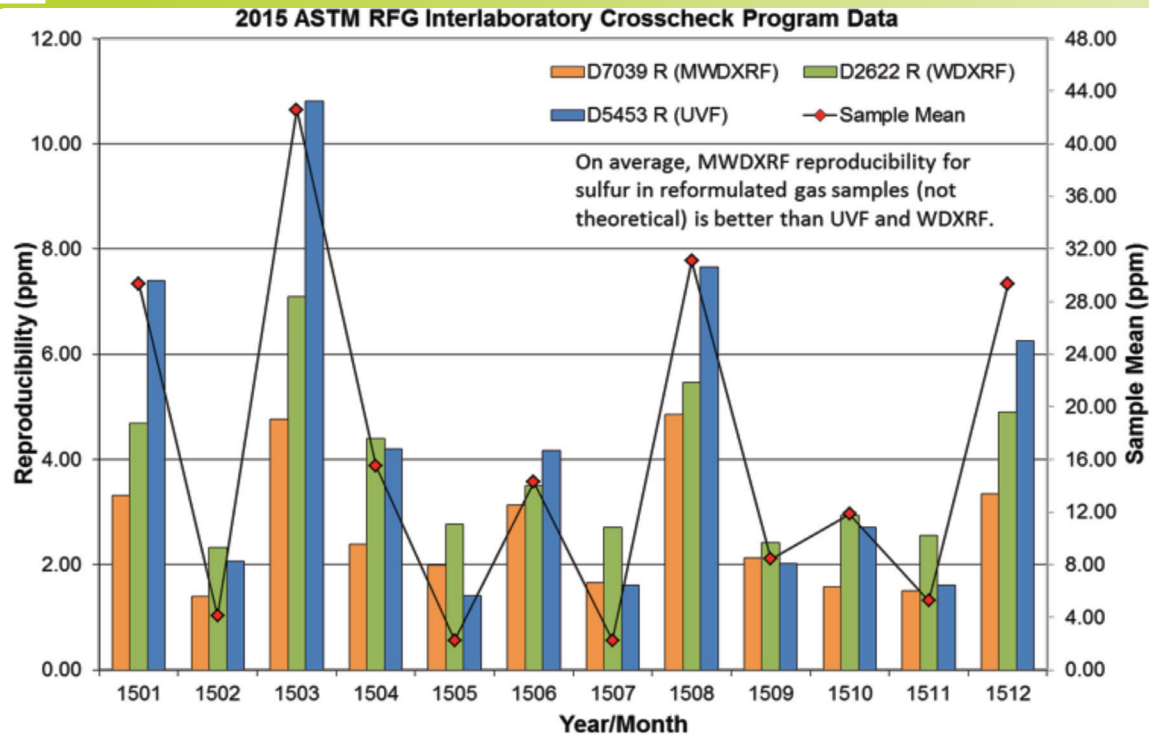


Figure 6. ASTM Interlab Crosscheck Data for Reformulated Gasoline 2015

Note that the precision statements for ASTM D7039 for the MWDXRF technique are based on the range of the method, 3.2 to 2822 ppm, which far exceeds the needs, when interested in measuring sulfur in finished product such as highway diesel or gasoline. If the results of Interlaboratory Study #761, gathered and analyzed in accordance with ASTM D6300 methodology for sulfur samples limited to ≤ 25 ppm S, it can be shown that the Repeatability (r) = 1.1 ppm and the Reproducibility (R) = 1.3 ppm.

Conclusions

When considering technologies for process analyzers, the most important characteristics of a good analyzer are reliable performance, a high degree of up time, superior stability, and good reproducibility, especially in the range of ≤ 10 ppm for sulfur. Having the lowest possible detection limit is not as valuable as having good precision at the control target. When used for

process control, small biases can be accounted for, as long as the process analyzer operates consistently within the control limits. An analyzer with simple construction, ease of maintenance, and ability to correlate closely with lab methods should be important in the selection process. Also important to remember is that no process analyzer is subject to "laboratory conditions" so the performance of the lab instrument may not be a good indicator of how the process version will perform in the field. A sulfur monitoring solution that minimizes or eliminates moving parts, gas cylinders, and scheduled maintenance and calibration events is ideal for process analyzers that cannot be maintained as frequently as lab equipment. When regulations limit the maximum sulfur concentration, a preferred technique is one that produces repeatable and reproducible results, while reducing the frequency an analyzer needs to be cross checked with laboratory measurements and allows refiners the confidence and flexibility to change process variables knowing that they have a precise measurement of the sulfur content in their process streams. While the EPA has sanctioned WDXRF as the primary testing technology, there is no process analyzer that measures strictly with this technique. However, process analyzers utilizing MWDXRF, a subset of WDXRF, are available and have been in service in the field since 2005. These analyzers were initially used for process control of sulfur in ULSD highway diesel but have since been used on naphtha streams and in gasoline blending. These analyzers have proven to be very reliable, simple to maintain, and correlate very closely with laboratory methods. The method does not require gaseous consumables so the cost of ownership is low. MWDXRF is the only WDXRF solution available for process. Validated in reproducibility tests, it is ready and proven for applications below 10ppm and even further (5ppm).

For additional information about how XOS can help with Tier 3 compliance, please visit our website at www.xos.com or contact us at info@xos.com.

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