Ultra Low Sulphur Analysis in Liquid Petroleum Products Using Monochromatic Wavelength Dispersive X-ray Fluorescence (MWD XRF)

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The U.S. Environmental Protection Agency (EPA) recently enacted new, lower sulphur level requirements in gasoline through the Tier 3 rule, part of a comprehensive approach to reducing the impact of motor vehicles on air quality and public health. The Tier 3 regulations are expected to be implemented in 2017, and call for reduced sulphur levels in the range of 10 ppm. There is still debate regarding the total cost and the scope of the implementation, but most would agree that refiners will need to make adjustments to their process infrastructure in order to meet this new specification. In the Tier 3 ruling, the EPA has designated wavelength-dispersive X-ray fluorescence (WD XRF) as the primary testing technology. This article discusses the ultra low sulphur analysis of petroleum products in the process and the available technologies for meeting changing regulations.

Introduction

The U.S. Environmental Protection Agency (EPA) has enacted new, lower sulphur level requirement in gasoline (Tier 3) and there is a renewed interest within the petroleum industry for measuring ultra-low level sulphur in fuels. The Tier 3 rule, part of a comprehensive approach to reducing the impacts of motor vehicles on air quality and public health, was signed in 2014 with the expectation of a 2017 implementation. The new regulations will lower the total sulphur limit from 30 ppm to 10 ppm for sulphur. These changes will require refiners to modify or install new infrastructure in their process units to meet this new specification. Refiners that process sour, heavy crudes may face even greater compliance challenges. To help ease the burden, the EPA has offered some relief in the form of compliance suspensions for smaller refiners, credits for past performance, and averaging of sulphur content nationwide. In order to make the transition as smooth as possible, it is critical to seek out the most efficient and precise technologies for measuring sulphur at these new ultra-low levels. For testing gasoline, the EPA has mandated ASTM D2622 as the primary compliance method. This method is based on wavelength dispersive X-ray fluorescence or WD XRF technology. In this paper, we will discuss the benefits of the WD XRF technology and the improvements made using doubly curved crystals. The use of two doubly curved crystals is the cornerstone of monochromatic wavelength dispersive X-ray fluorescence (MWD XRF). MWD XRF technology allows for improved reproducibility and a greater signal-to-background (S/B) ratio over traditional WDXRF, enabling refiners to better control their sulphur-removal processes and hold sulphur levels in finished product to tighter limits.

Total Sulphur Methodologies and Technologies

There are a number of different technologies available on the market for testing sulphur 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 analysers 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 Sulphur Methods

ASTM Method	Technology	Range	Scope Fuel Types
D2622-10	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, gasohol, and biodiesel
D4294-10	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, gasohol, biodiesel, and other petroleum products
D5453-12	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. 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.
D7039-13	MWD XRF	3 – 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 the MWD XRF technology. The high performing optics coupled with a lower power X-ray tube allow for a low maintenance, highly precise technology. MWD XRF is a simplified and highly robust X-ray technique which provides sub-1 ppm sulphur detection. An MWD XRF analyser engine (Figure 1) 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 fuel cell. The monochromatic primary beam excites the sample and secondary characteristic fluorescence X-rays are emitted. The second collection optic collects only the characteristic sulphur X-rays that are then focused onto the detector. The analyser engine has no moving parts and does not require consumable gasses or high temperature operations. MWD XRF eliminates the scattered background peak caused by the x-ray tube and improves 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 crystal allows for a small-area x-ray counter, which results in low detector noise and enhanced reliability.

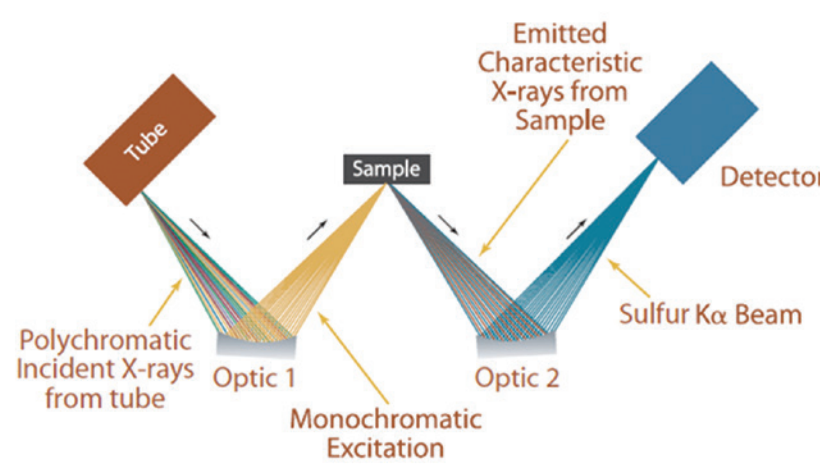

Figure 1 – Typical MWD XRF Setup

The WDXRF technique has been accepted practice for measuring sulphur in petroleum liquids for many years. However, with regulations for highway diesel to be 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 sulphur 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 sulphur 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 (sulphur) but low enough to minimize back 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 onto a detector. Acting

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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 onto 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. This in turn results in a cleaner fluorescence signal of the sample (far less scattering), which is then directed onto another doubly curved crystal for selecting only the characteristic energy of the element of interest to be diffracted onto 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 10X over WDXRF. It also allows use of a much lower power X-ray tube.

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

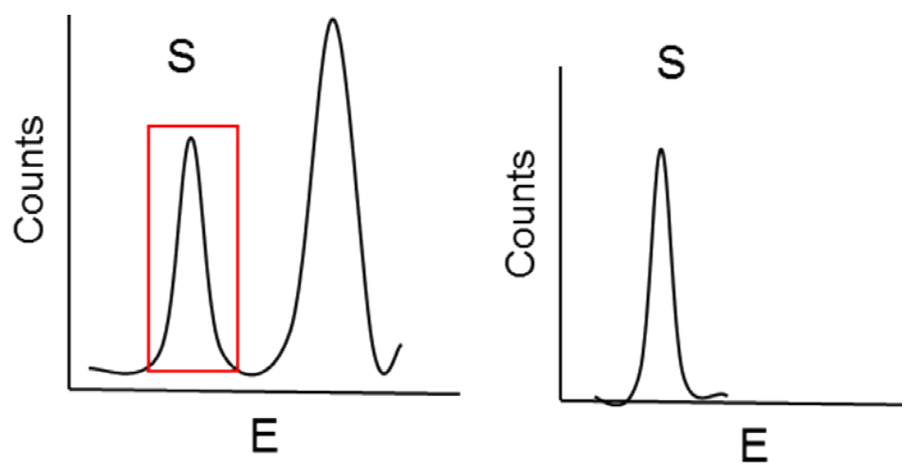

Figure 2 – (L) Sulphur Signal from sample excited by monochromatic excitation X-rays

(R) Monochromatic Sulphur Signal incident upon detector off collection DCC

Value of Precision

ASTM methods such as D7039 typically include full precision statements that include a repeatability and reproducibility component. Repeatability (r) is typically the variation of measurements 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, the reproducibility becomes critical because the reproducibility of the instrument will have an obvious impact of the total process reproducibility. If the process can be continuously and quickly monitored, variation can be identified and optimisation can be handled. As compared with the other methodologies in Figure 1, D7039 offers superior reproducibility from 5-10ppm which is critical for the Tier 3 mandate. This R value can help a refiner justify the economics of installation quickly when as optimisation can be achieved faster.

Note that the precision statements for ASTM D7039 for the MWDXRF technique are based on the range of the method, 3.2 to 2822 ppmw, which far exceeds the needs when interested in measuring sulphur in finished product such as highway diesel or gasoline. If the results of Interlaboratory Study #761, gathered and analysed in accordance with ASTM D6300 methodology for sulphur samples limited to 25 ppm S, it can be shown that the Repeatability (r) = 1.135 ppm and the Reproducibility (R) = 1.317 ppm.

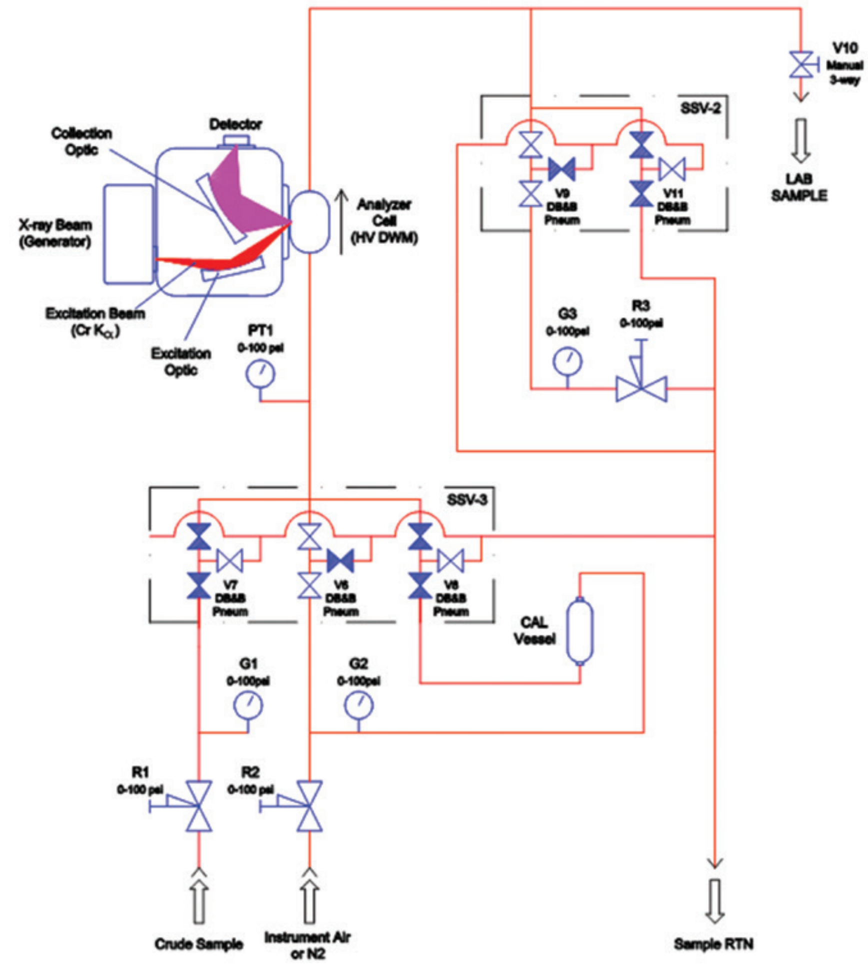

Figure 3 – Applied MWDXRF Process Analyser

Conclusion

When considering technologies for process analysers, the most important characteristics of a good analyser are reliable performance, a high degree of up time, superior stability, and good Reproducibility, especially in the range of 10-12 ppm for sulphur. 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 analyser operates consistently within the control limits. An analyser 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 analyser 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. When regulations limit the maximum sulphur concentration, a preferred technique may be one which will occasionally give a "false high" reading, creating a need for the analyser to be cross checked, over one that erroneously reports a low result and blindly steers the process towards out spec product.

While the EPA has sanctioned WDXRF as the primary testing technology, there is no process analyser that measures strictly with this technique. However, process analysers utilising MWDXRF, a subset of WDXRF, are available and have been in service in the field since 2005. These analysers were initially used for process control of sulphur in ULSD highway diesel but have since been used on naphtha streams and in gasoline blending. These analysers 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 for process available. Proven in Reproducibility tests, it is ready to go for applications below 10ppm and even further (5ppm).

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Multiple X-ray Technologies Integrated in Groundbreaking Spectrometer

In a significant announcement at Pittcon 2015, **PANalytical** (the Netherlands) has revealed a revolution in X-ray fluorescence spectrometry. With up to three complementary technologies on one multi-functional XRF platform, the new Zetium is set to change the way scientists think about XRF analysis. The measurement platform of Zetium holds both wavelength dispersive (WD) and energy dispersive (ED) cores integrated by SumXcore technology in one instrument. The Petro edition of Zetium can also include a small spot analysis tool for fast element distribution mapping, and is pre-calibrated to meet the regulatory requirements of the petrochemical industry.

This unique combination of technologies not only matches the traditional needs of XRF users, but offers a range of new possibilities. For example, measuring ED- and WDXRF simultaneously collects all the data on a sample in one run, cutting experimental time by up to half compared to running two sequential analyses. The Petro edition of Zetium is pre-configured to deliver results compliant with ISO and ASTM standards, through a choice of compliance modules. Zetium is designed to set new standards in terms of analytical power, usability and sustainability. The system is the successor to PANalytical's highly successful Axios range of spectrometers and this heritage of proven technology underpins the new analytical platform.

As well as the Petro edition, PANalytical has created four other industry-specific editions: Cement, Polymers, Metals and Minerals, as well as an 'Ultimate' edition. Each is available with a choice of four enhanced performance packages for: improved speed and throughput, performance enhancement, robustness and uptime, and flexibility.

The hardware advances in Zetium have been matched by an enhanced software framework and user interface. SumXcore technology is the software and hardware at the heart of Zetium, integrating the system's cores to deliver advanced performance coupled with maximum task flexibility. Ease of use for even non-expert users has been prioritized through the intuitive, task-oriented user interface and the integrated intelligence of the Virtual AnalystTM, which provides guidance on the optimal setup for each experiment.

"Zetium offers a unique combination of possibilities that put it in a class of its own for analytical power, speed and task flexibility," said Simon Milner, Product Marketing Manager for XRF, PANalytical. "And the system has been designed to allow customers to take full advantage of all our innovations. Zetium is a great demonstration of PANalytical's philosophy of elemental excellence – our focus is firmly on providing the best tools to help our users excel within their businesses."

For More Info, email: 34042pr@reply-direct.com